



**Chemistry**

AS / A Level Year 1 | WJEC | 1410/2410



2015 specification  
first exams in 2017 (2016 for AS)

# Stretch and Challenge Articles

for AS / A Level WJEC Year 1 Chemistry

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# Teacher's Introduction

This resource contains 11 'Stretch and Challenge' articles, written to stimulate and inspire able WJEC AS / A Level Chemistry students.

While the material covered is largely beyond the scope of the AS / A Level course, each article is linked to a topic from the specification, as outlined on the 'Specification information' page. This allows students to apply and reinforce their existing knowledge in unfamiliar situations, while also learning new concepts and skills. This pack covers the first year of the course, and includes physical, inorganic and organic chemistry content.

Each article is between 1,500 and 2,000 words, and is expected to take students around 30 minutes to read. Following the article, several questions are provided, divided into three groups:

- **Comprehension questions**, which encourage students to review the article in order to cement their understanding of new ideas.
- **Application questions**, which prompt students to think more deeply about the article, and to apply concepts.
- **'Taking it further' questions**, which invite students to research and make notes on additional aspects of the topic. Some questions ask students to choose an area to explore, allowing them to delve more deeply into the areas of chemistry that most interest them.

Questions in the first two groups are fairly short, and are suitable as classwork. Students could tackle them individually, in groups, or as a class. Suggested answers for the questions are provided for each article. 'Taking it further' questions are envisaged as homework tasks, though students could discuss and share their findings in class.

While the articles are intended to appeal to any enthusiastic Chemistry student, they would be particularly suited to those hoping to pursue the subject at a higher level and will provide ample talking points for any admissions interviews.

We hope you enjoy reading and using this resource.

*October 2021*

## List of articles

Article number	Topic	Article title
1	Redox	Redox reactions in biology
2	Electronic structure	What are orbitals?
3	Structure and bonding	Boron – breaking the rules of bonding
4	Group 2	Magnesium – more than a silver ribbon
5	Equilibrium	Haemoglobin – winning the equilibrium
6	Kinetics	Rates of reaction – how not to be scared of mathematical models
7	Mechanisms	Expanding the chemistry of alkenes
8	Halogenoalkanes	A closer look at nucleophilic substitution
9	Alkenes and isomerism	The chemistry of vision
10	Organic – general	Solvents – making solutions
11	Analysis	Springing into action – the theory behind infrared spectroscopy

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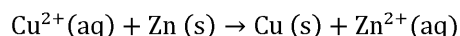


# Redox reactions in biology

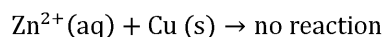
Despite often being taught as separate subjects at school, chemistry and biology are intertwined. From acids to adrenaline, DNA to dopamine, life depends on molecules and the chemical reactions between them. Given how common redox reactions are in the lab, it is hardly surprising that they are also common in biology. In this article, you will meet new ideas that are relevant to redox reactions in general and in a biological context. In doing so, you will discover how changes of oxidation state are not just being mere arithmetic, sustain organisms across the globe.

## Reduction potentials

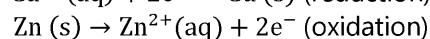
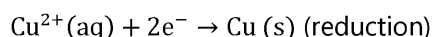
When a sheet of zinc is left lying in copper(II) sulfate solution, the zinc reduces the copper ions:



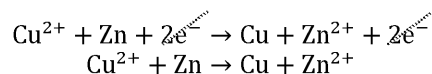
When a copper sheet is left lying in zinc sulfate solution, nothing happens.



In your work on redox so far, questions have probably specified which direction a reaction goes. If you weren't provided with this information, though, would you know? Yes, but we will need some new concepts if we are to do it. Firstly, redox reactions can be split into two **half-equations**, one representing the reduction process in terms of electrons and the other the oxidation process similarly. When the half-equations are added together, the electrons cancel out. For the reaction between copper ions and solid zinc, the half-equations are:

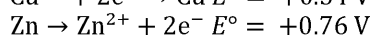
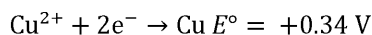


Adding them together:



If we were interested in the oxidation of solid copper or the reduction of zinc ions, we would use the relevant half-equation.

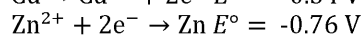
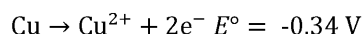
The energetic favourability of a redox process is measured by a value called the **redox potential** and with units of volts. A positive redox potential indicates a favourable process, and the more positive the redox potential, the more favourable the process. In the same way that adding the half-equations gives the overall reaction, adding their redox potentials gives the redox potential for the overall reaction,  $E_r^{\circ}$ .



$$E_r^{\circ} = 0.34 + 0.76 = +1.10 \text{ V}$$

Since the reduction and oxidation processes are both favourable, it makes sense that the overall reaction is also favourable as well.

Just as a half-equation for a redox process is flipped to show the reverse process, the redox potential is also flipped too. Thus, a process that is favourable in one direction will be unfavourable in the other. For the reaction between zinc ions and solid copper:



$$E_r^{\circ} = -0.34 + (-0.76) = -1.10 \text{ V}$$

The redox potential is negative, meaning that the reaction is unfavourable and does not occur. When listing redox potentials, it is conventional to give the redox potential for the reduction half-equation, whether the species is being reduced in the reaction being considered. As a result, we refer to **reduction potentials**.

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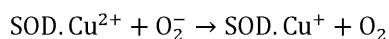
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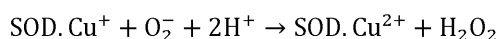
### Case study 1: superoxide dismutase

A paradox lies at the heart of human biology: the oxygen we need to survive has to be toxic to our cells. Under extreme conditions, breathing pure oxygen can even be fatal. (For normal air is oxygen.) The culprits are **reactive oxygen species**, derivatives of oxygen and other components of the cell in an uncontrolled fashion.

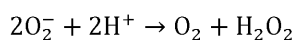
One notable reactive oxygen species is the superoxide ion,  $O_2^-$ . Here, an oxygen molecule has gained an electron, and has been reduced. The ion is eliminated by an enzyme named superoxide dismutase (SOD), which contains  $Cu^{2+}$  ions. First, one superoxide ion is oxidised back to molecular oxygen, and a copper ion is reduced:



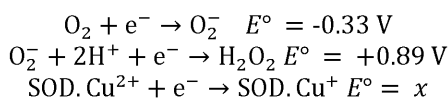
Then, another superoxide ion is combined with protons to form hydrogen peroxide, and  $Cu^{2+}$  in the process, ready to begin the cycle again:



The overall reaction is:



(Hydrogen peroxide is itself a reactive oxygen species, and is removed by another enzyme.) The half-equations involved are shown below, along with some reduction potentials:



Though the reduction potential of the  $Cu^{2+}$  ion in superoxide dismutase has been documented, it is listed as  $x$ . This is because, as an exercise, we will try to place limits on the value using the data already given. We know that, for a reaction to be favourable,  $E_r^\circ$  must be positive. For the first reaction, we change the sign of the  $O_2/O_2^-$  reduction potential and add it to the  $Cu^{2+}/Cu^+$  reduction potential:

$$\begin{aligned} E_r^\circ &> 0 \\ x + (+0.33) &> 0 \\ x &> -0.33 \text{ V} \end{aligned}$$

For the second reaction, we change the sign of the  $Cu^{2+}/Cu^+$  reduction potential and add it to the  $O_2^-/H_2O_2$  reduction potential:

$$\begin{aligned} E_r^\circ &> 0 \\ 0.89 + (-x) &> 0 \\ x &< 0.89 \text{ V} \end{aligned}$$

Taken together, these results tell us that  $x$  must be greater than  $-0.33 \text{ V}$  and smaller than  $0.89 \text{ V}$ . The reduction potential of the superoxide dismutase is to perform both reactions. Does this fit with experimental observations? The reduction potential of the  $Cu^{2+}$  ion in superoxide dismutase has been recorded as between  $+0.12 \text{ V}$  and  $+0.25 \text{ V}$ .

One of the remarkable features of enzymes is that they can carefully tune the redox potential of the active site, by placing a charged group next to it. For instance, placing a positive charge next to a copper ion is destabilising, due to electrostatic repulsion. Lowering the charge on copper would make the reduction to  $Cu^+$  more favourable.

The overall reaction is favourable. The enzyme is a dismutase. The reduction potential of the enzyme is  $E_r^\circ$ . Yes, it is a dismutase. The enzyme is a dismutase. The overall reaction is favourable. While the enzyme is a dismutase.

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## Oxidation states of carbon

Up until now, both in your lessons and in this article, you have focused on assigning **inorganic** compounds, defined by their lack of carbon atoms; the chemistry of life, overwhelmingly on **organic** molecules, which do contain carbon atoms. Thankfully we can use to establish the oxidation state of the carbon atoms in organic molecules.

1. Carbon-carbon bonds, single or double, do not affect the oxidation state
2. Each carbon-hydrogen bond decreases the oxidation state by 1
3. Each carbon-oxygen single bond increases the oxidation state by 1
4. A carbon-oxygen double bond increases the oxidation state by 2

If the average oxidation state of the carbon atoms in a molecule increases, the molecule has been **oxidised**; if the average oxidation state decreases, the molecule has been **reduced**. As such, oxidation involves the loss of carbon-hydrogen bonds and/or the formation of carbon-oxygen bonds, with the reverse true for reduction.

Let's try these rules out, starting with ethane.

Each carbon atom forms one single bond to another carbon and three single bonds to a hydrogen atom, leaving it with an oxidation state of -3. Next, we'll consider ethene.

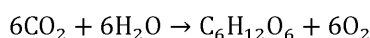
Now, each carbon atom forms one double bond to another carbon and two single bonds to a hydrogen atom, giving it an oxidation state of -2. Finally, we turn to ethanol.

The carbon atom on the left is identical to an ethane carbon, with an oxidation state of -3. The other carbon atom forms one single bond to a carbon atom, two single bonds to a hydrogen atom and one single bond to an oxygen atom. As a result, it has an oxidation state of -1, and the average oxidation state for a carbon atom in ethanol is -2.

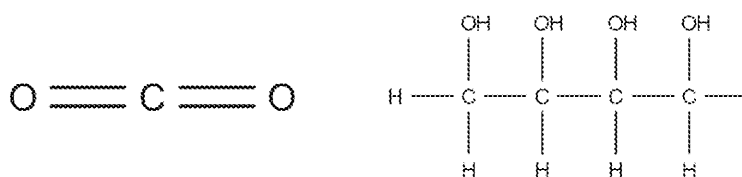
In summary, the conversion of ethene to ethane would be a reduction (-2 to -3; two carbon-hydrogen bonds formed), and the conversion of ethane to ethanol would be an oxidation (-3 to -2; one carbon-hydrogen bond lost, one carbon-oxygen bond gained).

### Case study 2: photosynthesis

Photosynthesis is carried out by plants, algae and some bacteria, and converts carbon dioxide and water into glucose ( $C_6H_{12}O_6$ ):



While the biological importance of oxygen is well-known, glucose is equally significant in the process of respiration. In terms of reactants and products, respiration is the reverse of photosynthesis: glucose and oxygen converted into carbon dioxide and water. However, animals do not produce glucose, and it is only introduced to a food chain through animals that eat plants. photosynthetic organisms also regulate the greenhouse effect and, by extension, the Earth's climate. Before looking more closely at photosynthesis, let's establish whether carbon dioxide is oxidised to glucose. The structures of both molecules are shown below.



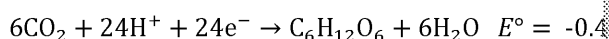
*The structures of carbon dioxide (left) and glucose (right)*

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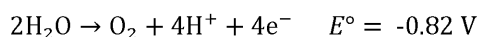
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The carbon atom in  $\text{CO}_2$  forms two double bonds to oxygen, giving it an oxidation state of +4. The middle four carbons have an oxidation state of 0, with the carbon–oxygen and carbon–hydrogen bonds cancelling each other out. The leftmost carbon forms two single bonds to hydrogen and one single bond to oxygen, and has an oxidation state of -1. The rightmost carbon has an oxidation state of +1, with one double bond to oxygen and one single bond to hydrogen. The average oxidation state of carbon in glucose is therefore 0, and carbon dioxide is *reduced* to glucose. The corresponding half-equation is:



The necessary electrons are obtained via the oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$ :



Using the redox potentials to calculate  $E_r^\circ$ :

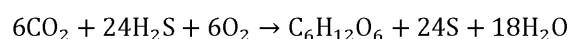
$$E_r^\circ = -0.42 + (-0.82) = -1.24 \text{ V}$$

Hmm... the result is negative, suggesting that photosynthesis is not favourable, yet we do it every day. What's going on? The key is that *unfavourable* does not mean *impossible*. It's like placing a ball at the top of a steep slope. Naturally, the ball will roll down the slope, but you need to push it. Returning to redox reactions, electrons can be made to flow in the opposite direction, if enough energy is supplied. In photosynthesis, this energy is provided by light. The fact that energy must be *taken in* for photosynthesis is consistent with the fact that energy is required to drive the reaction.

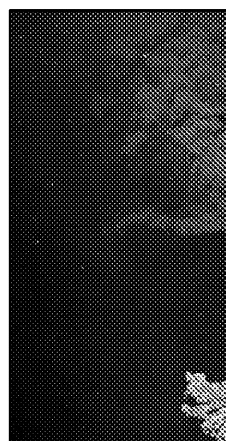
### Dining in the dark

The deep ocean is home to many weird and wonderful creatures, including the giant squid, despite a total lack of sunlight. Clearly photosynthesis cannot take place under these conditions. So where do the sugars necessary for life come from? In most cases, they fall from the upper layers of the ocean as waste matter and the remains of dead organisms. Surviving off these scraps is how many organisms live on the ocean floor. Scattered throughout this marine wasteland, though, are hydrothermal vents where ecosystems thrive in comparison. These communities depend on **chemosynthesis**. Instead of carbon dioxide into sugars without light. They rely solely on chemical reactions.

The reaction pathways used in chemosynthesis vary, but many involve oxidation of hydrogen sulfide,  $\text{H}_2\text{S}$ , to elemental sulfur. The overall equation for this class of reactions is given below.



Hydrogen sulfide is pumped into the water by geological formations known as hydrothermal vents, where water heated in Earth's crust bursts through the seabed. It is thought that life on Earth might have begun near these structures, with chemosynthesis supporting its development until photosynthesis evolved.



A hydrothermal vent.

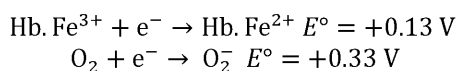
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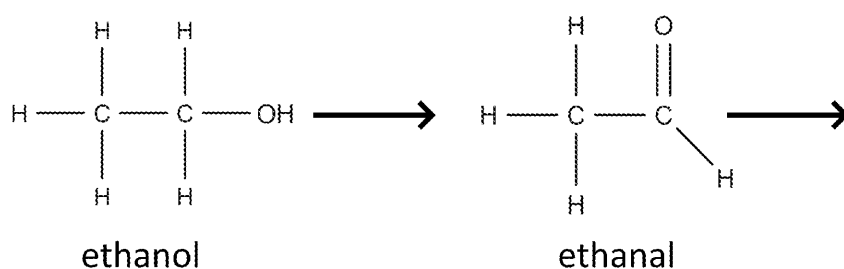


## Comprehension questions

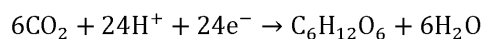
- Explain the meaning of the following terms:
  - reduction potential
  - enzyme
  - inorganic
  - chemosynthesis
- Haemoglobin (Hb) is a protein that transports oxygen around the body. Occasional haemoglobin reacts with oxygen to form a superoxide ion. The relevant half-potentials are given below.



- Write the overall reaction equation.
  - Which species is being reduced and which is being oxidised?
  - Calculate  $E_r^{\circ}$ . Is the reaction favourable?
- During the metabolism of alcoholic drinks, ethanol is converted first into ethanal



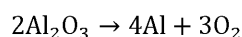
- Determine the average oxidation state of the carbon atoms in ethanol and ethanal. Which carbon is oxidised or reduced in the first reaction? What about ethanal in the second reaction?
- Based on the change in the average oxidation state of carbon, explain why 24 electrons are needed in the following half-equation.



## Application questions

- There are several ions that contain only oxygen. By far the most common is the oxide ion,  $\text{O}^{2-}$ . In the superoxide ion,  $\text{O}_2^{-}$ , oxygen has an oxidation state of -1. Deduce the oxidation state of oxygen in the following ions:
  - peroxide ion,  $\text{O}_2^{2-}$
  - dioxygenyl ion,  $\text{O}_2^{+}$
  - ozonide ion,  $\text{O}_3^{-}$
- While calculating  $E_r^{\circ}$  for photosynthesis, we did not multiply the potential of the half-equation by 6, even though the half-equation was multiplied. Based on the fact that volts = joules/coulomb, explain why. (Hint: coulomb is the SI unit for charge.)
- In the article, you learned that unfavourable reactions can be carried out by supplying energy. This energy is often electrical.
  - What name is given to the process of supplying electrical energy to drive reactions? (You might remember this from GCSE. If not, look it up.)

One application of this process is isolating aluminium from its ore, bauxite.



- Write balanced half-equations for this reaction.

## Taking it further

- Research other redox reactions in biology. Choose **four** reactions and write a short paragraph about each one, including what type of organisms carry out the reaction, which species are involved and why the reaction is important.

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# What are orbitals?

Throughout school, Chemistry students are introduced to different models described in an atom, each more nuanced and more complex than the last. When first introduced as a negative particle that orbits the nucleus, and then sometime later described as a negative particle that orbits the nucleus. By A Level, the idea of circular orbits is replaced with atomic orbitals of different shapes. But what actually is an orbital – is it anything more than a description of the shapes? This article will explore electrons a bit further and bring in quantum theory to gain a better understanding of a particle that is central to chemical reactions.

## A bit of history: wave-particle duality

The electron was first discovered in 1897 by J Thomson. He used a heated cathode (negative electrode) to produce a 'cathode ray', and then used the fact that this beam could be deflected by discrete amounts in an electric field to show that the ray was actually a beam of negative particles, since the beam was attracted towards a positive electrode (anode). We now understand that by heating the cathode, Thomson was ionising the outer electrons in the metal that formed the beam. The degree of deflection also allowed Thomson to work out the charge-to-mass ratio of an electron (e/m).



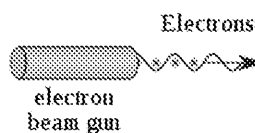
Thomson's work was followed by the work of Robert Millikan in 1906. Millikan designed an experiment in which he used tiny negatively charged oil drops to work out the mass of an electron. He used the fact that the oil drops would fall due to their weight caused by gravity, but then balanced this out by an electric field above the oil drops pulling them upwards. He adjusted the electric field causing the oil drops to be suspended in mid-air. This meant that for an individual oil drop:

$$F_{\text{down}} = mg = F_{\text{up}} = qE$$

So:  $mg = qE$

By working out the mass of an oil drop (m), and knowing E (the field strength that caused the oil drop to be suspended) and g (acceleration due to gravity), Millikan was able to calculate q, the charge of the oil drop. This was always a multiple of  $1.60 \times 10^{-19}$  C (coulombs), meaning that the charge of the oil drop was exactly that number. This is e, the charge of one electron. Because Thomson and Millikan was then able to work out m, the mass of an electron, as well. All of this work led to the discovery of a particle with a mass of  $9.11 \times 10^{-31}$  kg and a charge of  $1.60 \times 10^{-19}$  C.

Fifty-five years later, Claus Jönsson showed that as well as being particles, electrons are also waves. By passing a beam of electrons through two slits, an interference pattern was observed – this only happens with waves. As a wave passes through a slit, diffraction occurs and the wave spreads out. If this happens with two slits, the two waves interfere with each other once they've passed through the slit, causing a distinctive pattern of where the waves interfere constructively (add together) and where they interfere destructively (cancel out).



The nature of electrons as both particles and waves is known as wave-particle duality. We treat electrons as particles when, for instance, we talk about electrons being things in solution during chemical reactions. Trying to explain this with waves is much more complicated. There is a limit to chemical understanding if the wave nature of electrons is ignored. This will be explored in the rest of this article.

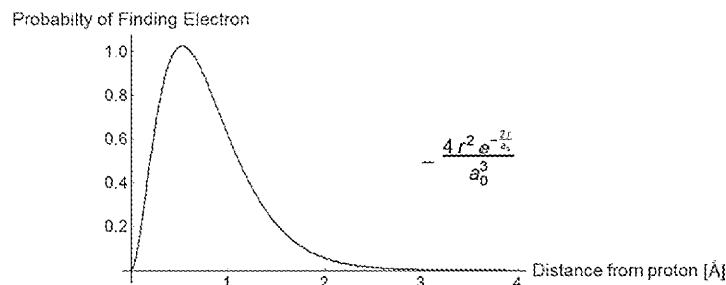
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# Orbitals

Because electrons are waves, the Bohr model of an atom with electrons orbiting a nucleus is insufficient – waves cannot be described like this. Instead, electrons are described using a probability pattern of an electron wave around the nucleus. The pattern is called the 'radial distribution function' shown below for a 1s orbital in a hydrogen atom. This pattern is the solution to a Schrodinger equation, and is an example of where the tools of mathematicians are used by physicists and chemists to understand a theoretical concept. The solution is included below.



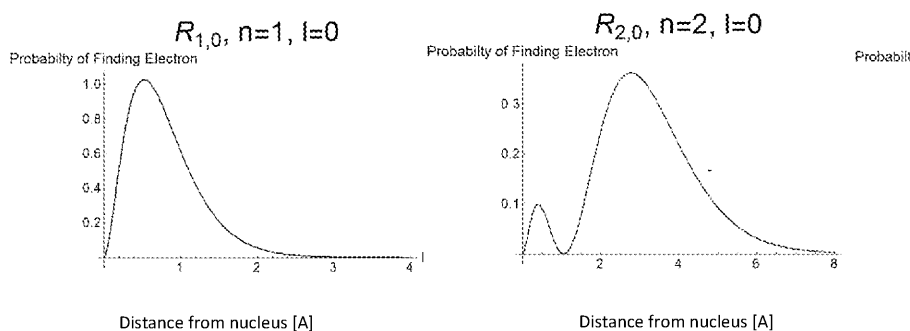
- The graph describes the probability of finding an electron wave at a certain distance from the nucleus.
- The probability of finding an electron is highest at the nucleus and decreases as the distance from the nucleus increases. This means that the electron is most likely to be found close to the nucleus. This means that the electron is most likely to be found within a certain distance from the nucleus. In mind, an electron is found within 90% of the electron's probability.
- The graph is a smooth curve that starts at 0 and approaches 0 as the distance from the nucleus increases.

This is the simplest orbital. To be able to distinguish between all orbitals, we need to use three quantum numbers, which describe the characteristics of the orbital an electron is in. These are:

- $n$ , the principal quantum number. This tells us what shell an electron is in.
- $l$ , which tells us the subshell (s, p, d, f)
- $m_l$  which tells us the specific orbital

## Comparing different orbitals

Each orbital has a different set of quantum numbers, and as a result has a slightly different probability distribution.



1s

2s

Each orbital has the same general characteristics described above but varies in the electron density from the nucleus, and in the presence of 'nodes' where the probability of finding an electron is zero. Comparing 1s with the 2s and 2p orbitals, the 1s probability peaks at a shorter distance from the nucleus, meaning that the electron density is highest at the nucleus. This is because the electron density is closest to the nucleus.

More interestingly, we see that the main peak for 2p is actually closer to the nucleus than the main peak of a 3d orbital. This electron density corresponding to these smaller peaks is called shielding. By the time we get to 4s there are three of these small inner peaks. This means that when averaged out 2s experiences a stronger attraction to the nucleus than 3d. This means that 2s is filled before 3d. These inner peaks are called shielding. By the time we get to 4s there are three of these small inner peaks. This means that when averaged out 4s experiences a stronger attraction to the nucleus than 3d. This means that 4s gets filled first (as in potassium) before 3d.

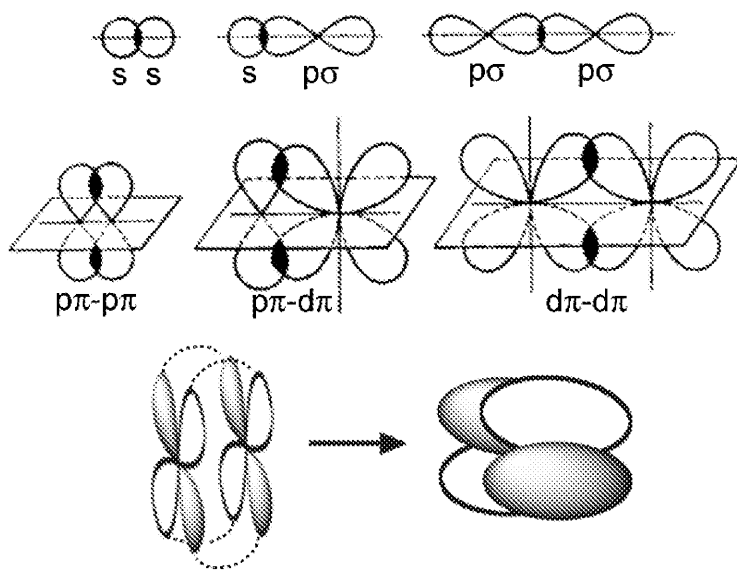
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## Orbitals and directionality

We can see that s orbitals are spherically symmetric. This means that when s orbitals are involved in a reaction it doesn't matter what direction another atom or molecule approaches from – there is no steric effect. With p orbitals, d orbitals, f orbitals, etc. this is no longer true. For orbitals to overlap to form a bond, another orbital must approach these orbitals from the right angle – there is a steric requirement. It also means that it is also possible to form bonds head-on (sigma/ $\sigma$  bond) or side on (pi/ $\pi$  bond) or even form delta bonds.



A delta bond involving two d orbitals

There is very low probability of finding the electron in this direction.

Because these p wave behaviour of that it should be same way that w different sound v music that has as waves but is differ process called 'hy that have charact

In carbon there are four electrons in the outer shell, but since 2s is lower than 2p, there would normally be two electrons in a spherical s orbital, two p orbitals each with an electron and an empty p orbital. How can carbon make four identical bonds? By mixing these four orbitals together to form four identical 'hybrid' orbitals. These identical orbitals then give the characteristic tetrahedral shape. Since these four orbitals are made from an s and three p orbitals it is called an 'sp<sup>3</sup> hybrid'.

All of these orbitals can now be modelled using computer programs based on the original equations for these orbitals. By doing this we can also see what happens over time when molecules react, observing how the orbitals change shape as the electrons move from one molecule to another. This is a brand-new way to 'see' chemistry – not at the macro level on the bench in a lab, but on a computer screen, where orbitals oscillate and alter as different species attract, repel and react. This is new territory and the future awaits for this 'computational chemistry'.

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## Comprehension questions

- Define the following terms:
  - Interference (of waves)
  - Orbital
  - Principal quantum number
  - Radial distribution
  - Hybridisation
  - Node
- In your own words, explain what is meant by wave-particle duality.
- Write a set of bullet points to summarise the contribution of Thomson, Millik understanding of electrons.
- In your own words, explain why treating electrons as if they were just particle explanations difficult.
- Why do p orbitals have directionality but not s orbitals?
- Why are 4s orbitals filled before 3d orbitals?

## Application questions

- Sketch the radial distribution of a 4s orbital. How many nodes does it have? you predict a 4d orbital would have?



- The orbital on the left above is a d orbital. Draw the  $\sigma$ -bond formed between
- To form a bond from two orbitals, the phases of the orbitals must match (this the 'up' parts of a wave and the 'down' parts of a wave). Suggest why the d could  $\sigma$  bond with an s orbital, but the d orbital on the right could not.
- The orbital on the right above is also a d orbital. Of the three p orbitals in a could successfully form a bond with this d orbital. Draw diagrams to support

## Taking it further

- Research and write a three-quarters-of a-page summary on computational chemistry in different fields.
- Research a bit more about the Schrodinger equation. Write a half-a-page summary contains and how it is used (hard!).

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# Boron - breaking the rules of

Like many areas of science, the concept of a 'chemical bond' is one that can be understood by a person in the street all chemical bonds could be the same, whereas a school student a few years will know, at least, that there are different types of bond, such as ionic. This student may also be familiar with the idea that ionic bonding involves the 'transfer' of electrons, whereas covalent bonding involves the 'sharing' of pairs of electrons – and that elements can have full/empty shells of electrons.

Boron, element number 5 in the periodic table, forces us to shift our understanding of the traditional view of ionic/covalent bonding. The chemistry of boron involves a mixing of ideas, and we should consider electrons as waves rather than particles – opening up a whole new area of chemistry and every rule of bonding that is taught in schools.

## Electron deficiency

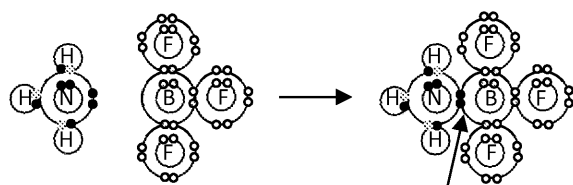
Because boron's outer electrons are only in the second shell, losing all three of them to form a  $B^{3+}$  ion is extremely unlikely, as a lot of energy would be needed to remove three electrons so close to the nucleus. Similarly, gaining five electrons to form  $B^{5-}$  would also take a lot of energy, meaning that boron does not form simple ionic compounds, and must rely on covalent bonding, at least in part.

- Boron has three electrons in its outer shell ( $1s^2 2s^2 2p^1$ ).
- This means it can form three 'shared pairs' of electrons.
- Three shared pairs of electrons in its outer shell gives it six electrons; two short of a 'complete octet'.

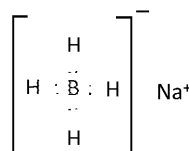
A compound such as boron trifluoride, with boron having only six electrons in the outer shell, breaks the 'octet rule' of elements having only full or empty shells in compounds. For this reason, we describe a compound such as  $BF_3$  as 'electron-deficient'; if given the opportunity it would be more favourable for boron to have a complete outer shell, and a compound like  $BF_3$  is, therefore, going to be a compound that is reactive with electron-rich compounds.

## Dative bonding

The obvious solution for a compound such as  $BF_3$  is to form a 'dative covalent bond' (also called a coordinate bond), where an atom, ion or molecule with a lone pair forms an extra bond. In this case, the extra electrons in the shared pair come from the other atom, ion or molecule.



*In this example, a nitrogen atom in ammonia ( $NH_3$ ) has a lone pair which it can use to form a coordinate bond. This forms the compound  $NH_3BF_3$ .*



Lewis dot structure of  $NaBH_4$

*Here, an  $H^-$  ion donates a lone pair to the  $BH_3$  ion, known as a dative bond.*

The second example above is a good example of where an electron-rich species, such as a hydride ion, forms a dative bond with an electron-deficient species like a  $BH_3$  molecule. This forms a coordinate bond. You will meet the borohydride ion,  $BH_4^-$  ion, in organic chemistry when it reacts with another compound in a reduction reaction (reduction is gain of electrons, and oxidation is loss of electrons). This transfer of  $H^-$  mimics the way reduction reactions often happen in nature, making it one of the most important artificial reducing agents to organic chemists.

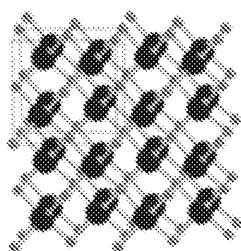
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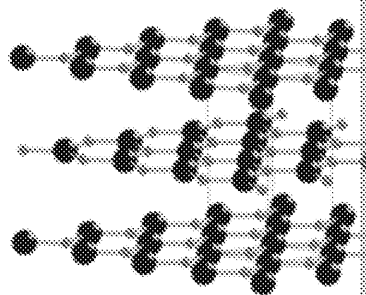


## Scratching diamond?

When boron bonds to nitrogen, the result is a bit special because a boron and nitrogen atom is **isoelectronic** (3 outer electrons + 5 outer electrons) to two carbon atoms ( $2 \times 4$  outer electrons), and therefore, the potential for boron/nitrogen compounds to be formed that are similar to diamond and graphite.



Cubic BN

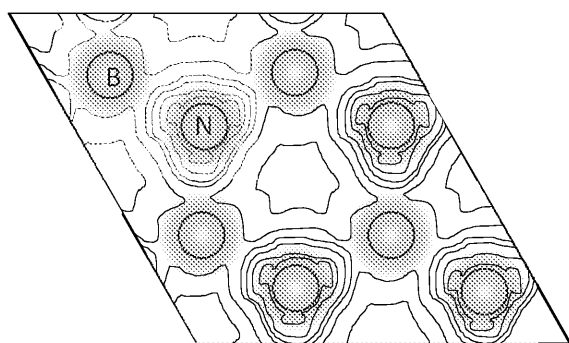


Hexagonal BN

Every carbon atom in diamond or graphite is equivalent to every other carbon atom and contributes four electrons to form four shared pairs. The exciting thing is that in diamond there is a degree of ionic character as well, not just traditional covalent bonds. This is because nitrogen is more electronegative than boron, creating a dipole in the B–N bond and making the boron atom slightly positive ( $\delta^+$ ) and the nitrogen atom slightly negative ( $\delta^-$ ). Having covalent and ionic (electrostatic) attraction can make a structure even stronger, and it has been found that hexagonal BN (diamond's structure), not diamond, is actually the hardest substance known to humankind. This has been definitively proven, however, and is still a matter of scientific debate.

In addition, this means that hexagonal BN, which is similar to graphite, has graphite-like properties (it is a lubricant when layers slide over each other) but is much more stable at high temperatures. This is due to the 'ionic/electrostatic attraction' adding to the strength of the covalent bond. Where there is a dipole–dipole forces between layers, the ( $\delta^+$ ) boron atoms on one layer of BN can attract the ( $\delta^-$ ) nitrogen atoms on the next layer, strengthening the structure. Hexagonal BN is, therefore, the lubricant used in long-range rifle bores when the bullets are shot explosively out of the rifle.

## Electrons as waves



An electron density map of hexagonal boron nitride

This mixing of ionic character in diamond has the limitations of drawing a sharp boundary between the two. It would be more useful to use the idea of thinking of electrons as solid particles. In the diagram above, the electron density around every carbon atom is identical. In the diagram above, the electron density is mapped in hexagonal BN, with the electron density around nitrogen (N) showing the higher electron density around the more electronegative atom.

We can compare this to a situation where the electron density is almost all on one type of atom. This situation we would call ionic bonding.

The difference between 'covalent bonding with ionic character' (as in the diagram above) and ionic bonding (where the electron density is on one type of atom) is ultimately slightly arbitrary. Covalent and ionic bonding are examples at either end of the same spectrum of bonding!

Maps of electron density like this also show the limit of the idea of electrons being particles. Thinking of electrons as waves allows us to think of electrons as spread over an area, with a higher amplitude in some areas than others. This is called wave–particle duality.

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## Banana bonds

When we start to think of a bond between atoms as an area of overlapping electron density (as in the map above), we can start to challenge the assumption that a bond is only between two atoms. This is a radical challenge to our understanding – but the chemistry of boron forces us to do this!

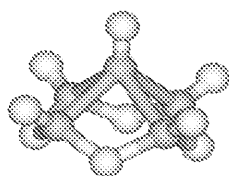
To recap so far, we have said that a simple molecule like  $\text{BH}_3$  would leave boron with only six electrons in its outer shell (three from boron, one from each hydrogen in a covalent bond). The most common solution to this is for another atom or ion to donate a pair of electrons to form a coordinate bond.

In diborane, the two electrons come from a B–H covalent bond in another molecule of  $\text{BH}_3$ . This creates the situation where a pair of electrons is shared between two atoms. This type of bond is called a 3-centre-2-electron (3c2e) bond. It is not possible to have the usual  $109.5^\circ$  bond angle in diborane, and instead the bonds form a shape

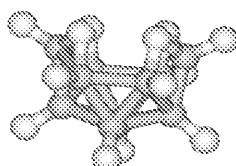
Unsurprisingly, it would be more stable if there were two covalent bonds, each with a pair of electrons, rather than the pair of electrons being shared across three atoms. Diborane is, therefore, rather unstable – to the point that it is explosive. It was considered as a potential fuel for rockets. Standard advice is for an evacuation area of one mile if there is a risk of

## Far-fetched chemistry – boranes

Once the idea of a covalent bond being a shared pair of electrons between two atoms is accepted, a whole range of wonderful molecules are possible. The limitation is that they will always be reactive. The images below show molecules made from boron and hydrogen using multiple 3c2e bonds and truly stretch the models of chemistry used at school! They are in their own area of chemistry, and they have also found a use in a type of cancer treatment.



$B_5H_9$



$B_{10}H_{14}$



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## Comprehension questions

- Write definitions for the following in your own words:
  - Electronegativity
  - Isoelectronic
  - Electron density
  - 3-centre-2-electron bond
  - Wave-particle duality
- Ammonium fluoride ( $\text{NH}_4\text{F}$ ) is an ionic compound containing covalent bonds explain what this means, and label any dative covalent bonds.
- A single beryllium chloride ( $\text{BeCl}_2$ ) molecule would be described as electron-deficient. Explain what this means.
- Explain in full why B-N is a polar bond and why it is isoelectronic to a Be-O bond.
- Why does boron nitride have different properties from diamond and graphite?
- What is the link between the bond angles in diborane and its reactivity?
- What is the link between an electron density map and the fact that electrons are delocalised in graphite?

## Application questions

- $\text{H}^-$  is a particularly reactive ion, even though it has a full outer shell. Suggest why it is more stable with an extra electron ( $\text{H}^-$ ) than any of the group 7 atoms that have formed a diatomic molecule.
- Describe an electron density map of graphite with its pattern, and its differences from diamond.
- Would a 3c2e compound be more likely to react with oxidising agents or reducing agents?

## Taking it further

- Research neutron capture therapy of cancer and draw a series of diagrams to show how it works.

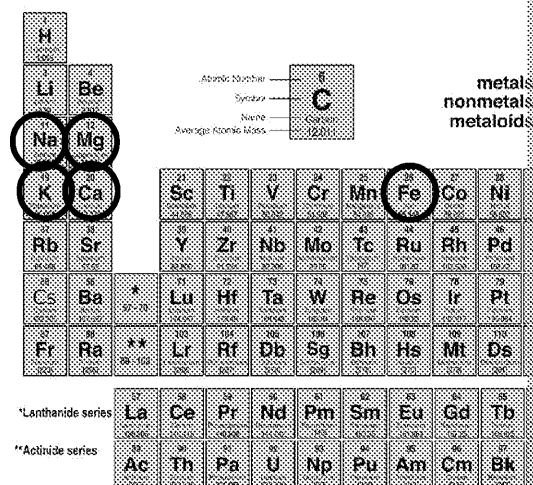
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# Magnesium – more than a silv

Among the elements most abundant in organic life, non-metals dominate, especially nitrogen. Metallic elements do, however, play a key role in biological systems, including sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ) and iron ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ). Of these metals, however, only magnesium and iron find common use in other areas. You will probably be aware of iron's importance in steel – which holds up both our buildings and the end of a teaspoon. You may also be aware of the key role of iron ions at the cell level: they carry oxygen to cells around the body, and carbon dioxide back to the lungs. Magnesium, like iron, but the variety of its roles in both organic and inorganic chemistry is impressive – and much of this relies on the principles you will cover in your study of group 2 at A Level.



The location of some metals in the periodic table

## Magnesium and life

Magnesium is the eighth most abundant element in Earth's crust, being slightly less than sodium and calcium, and less than half as abundant as iron and aluminium. Despite its abundance, it is the most abundant metal across all cellular life. The reason for this is linked to the origin of life: magnesium clearly had properties that made magnesium suited for incorporation into cells.

### Staying in solution

Magnesium ions have a stronger electrostatic attraction to water molecules (and hydroxide ions) than the elements of group 2 below magnesium, which means they are more soluble. This is because magnesium ions are smaller, and can be thought of as having a 'more concentrated'  $2+$  charge, which attracts the partial negative charge ( $\delta^-$ ) on oxygen in water molecules more strongly.

Because calcium ions are less soluble than magnesium ions, they are more likely to form solid precipitates with other ions found in water, such as sulfate ions and carbonate ions. This explains why magnesium sulfate is soluble whereas the sulfates of group 2 below it are much less soluble (as you learn at A Level), and why calcium has a common role in living organisms as part of solids such as calcium carbonate (which makes up shells, coral and eggs) and a form of calcium phosphate which makes up bones.

Sodium ions and potassium ions are soluble, like magnesium ions, but form much more complex molecules due to their  $1+$  charge. The reason they are soluble in water, despite their higher charge than the  $2+$  ions in group 2, is that the group 1 ions do not form comparably strong precipitates with other ions or molecules either, and, therefore, remain dissolved in water instead of

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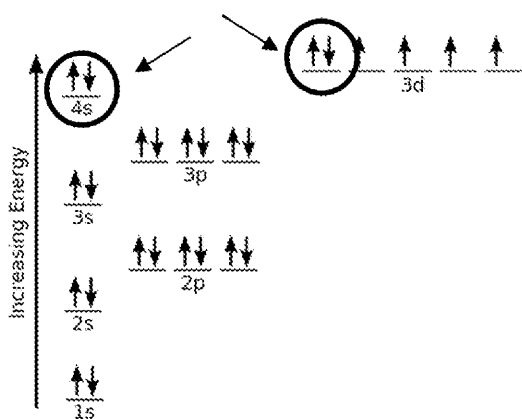
## Transport

The ability of magnesium to bind well to water molecules means it has the potential to be transported across membranes, a key trait in early cellular life. Sodium and potassium ions most commonly pass in and out of cells without contributing to any structures once inside the cell – they just pass out again (movement that is key to nerve transmissions). However, because magnesium can form stronger electrostatic attractions, magnesium ions can then bind to other substances containing electronegative oxygen or nitrogen atoms. This means transported magnesium ions can be incorporated into important structures inside the cells, such as chlorophyll in plants, or bind to substances to allow them to carry out their role; for example, binding to ATP (our 'energy currency') in many organisms.

## Fe vs Mg

Iron 2+ ions ( $\text{Fe}^{2+}$ ) behave in a similar way to magnesium ions – they form relatively strong bonds with water, and can then also form new electrostatic attractions with other molecules containing nitrogen or oxygen atoms inside a cell. Both Fe and Mg are essential in many forms of life. Two key differences between the two are:

- 1) their size – magnesium's outer electrons are in a 2p subshell, whereas
- 2) and iron's ability to be oxidised into other ions, mainly  $\text{Fe}^{3+}$ . This change involves  $\text{Fe}^{2+}$  losing an electron to form  $\text{Fe}^{3+}$ , which it often regains to form  $\text{Fe}^{2+}$ .



*Iron electronic structure – the 4s electrons are lost easily, but a 3d electron may also be lost and regained, meaning iron forms both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  commonly*



*Magnesium electronic structure – the 3s electrons are lost easily, but the 2p electrons are held more strongly*

The extra electron that  $\text{Fe}^{2+}$  loses when it forms  $\text{Fe}^{3+}$  can allow other chemical reactions than they would have done otherwise, meaning that  $\text{Fe}^{2+}$  ions can play a role as an oxidant and reductant.  $\text{Mg}^{2+}$  does not lose or gain electrons easily – the 3s electrons are lost to form  $\text{Mg}^{2+}$  as they are further away and not held strongly, but losing subsequent electrons is very difficult due to their proximity to the nucleus. This means that  $\text{Mg}^{2+}$  ions are not as chemically reactive as magnesium metal is (magnesium metal is very reactive). There are many examples of biological molecules that are chemically inert if they are to perform their function (e.g. the backbone of DNA and the cell membrane), and, therefore,  $\text{Mg}^{2+}$  is much more suited in these situations than  $\text{Fe}^{2+}$ .

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## Magnesium as a metal

Most people associate magnesium metal with the strips that get burned in Chemilights (which produce a bright white light (while the teacher tells the class not to look directly at it!). It also gets used in test tubes of hydrochloric acid, watching it bubble and lighting the gas to produce a small flame of hydrogen. Not many people think of magnesium as being a metal that is useful in industry, but it is in fact a metal that has a very important set of properties.

### Density

The metals in the top left of the periodic table have in common a high reactivity, but a low molecular weight. Magnesium is the least reactive of the metals in groups 1 and 2 (except for beryllium, which is quite different from the other elements), and is by far the most common of the light metal alloys, partly due to its lower reactivity. Only iron and aluminium are more common in structures, and magnesium is normally used to form an alloy with these metals. One of the advantages of magnesium with these metals is that its low density allows for lower-density alloys, which are used in construction, transport, electronics and many other areas of technology where a light metal is needed.

### Elektron

The risk with using magnesium in alloys is that the metal itself is very reactive, but it forms a protective layer of magnesium oxide in a vigorous reaction. This is very rarely a problem in alloys, as shown by the fact that magnesium – has been used to make engines for the aerospace and car industry, Elektron Ltd company having produced the alloy in Manchester since 1936.

On two occasions, however, the flammability of the magnesium has meant that Elektron has hit the headlines. Firstly, in World War II, when the low-density Elektron was used to make bomb casings. The lighter-weight bombs could be transported in higher numbers, and when they exploded on landing the burning magnesium burned through metal, reacted with any water poured on it, and continued to react for over 15 minutes. In the 1955 Le Mans race the same effect was observed with horrifying consequences when a car with an Elektron engine crashed and its fuel tank exploded, causing the Elektron engine to subsequently explode and shower the crowd in burning magnesium. Unwitting stewards attempted to put out the fires with water, making them much worse and creating flames which burned for several hours. Sadly 85 spectators were killed, as well as the driver of the car.

Modern research continues to work on developing magnesium alloys that are resistant to fire, safe to use by varying the amount of magnesium in the alloy, and including other elements to reduce the likelihood that magnesium will react with oxygen.

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## Comprehension questions

1. Explain what the following terms mean:
  - a) Electronegative
  - b) Partial charge
  - c) Precipitate
  - d) Molecular weight
  - e) Alloy
2. Why are barium ions ( $\text{Ba}^{2+}$ ) less soluble in water than the ions of the element?
3. Summarise the key properties of a)  $\text{Mg}^{2+}$  ions and b) Magnesium metal.
4. Summarise the key reasons why  $\text{Mg}^{2+}$  ions are the most common metal ion in seawater, despite magnesium not being the most common metal on Earth.

## Application questions

5. Enthalpy of hydration is the energy released when one mole of a gaseous metal ion is hydrated. The enthalpies of hydration of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  are, from largest to smallest:  
 $-1926 \text{ kJ mol}^{-1}$ ,  $-406 \text{ kJ mol}^{-1}$ ,  $-320 \text{ kJ mol}^{-1}$   
Match the values to the metal ions, explaining your reasoning.
6. Suggest the benefits and risks of using lithium in alloys compared to magnesium.
7. Suggest the main environmental advantage of using magnesium in engines and alloys, based on its position from the centre of the periodic table.
8.  $\text{Mg}^{2+}$  ions can act as catalysts, but often in a different way to  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions. Explain the difference between ions acting as a **cofactor**. Find out what this means, and write an explanation of the importance of  $\text{Mg}^{2+}$  ions acting as a cofactor. Find out a biological example of when this is important.
9. Magnesium ions can act as **Lewis acids**, which allow pH to be lowered in a gel, rather than by releasing lots of  $\text{H}^+$  ions like Bronsted–Lowry acids which are Lewis acids. Explain what a Lewis acid is, and explain why a Lewis acid (such as  $\text{Mg}^{2+}$ ) would slightly lower the pH of a gel.

## Taking it further

10. Copper ions are also important to life. Research some of the key roles that copper ions play in life, and what the key properties of copper ions are that allow it to perform its role well.

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# Haemoglobin - winning the equilibrium

Haemoglobin is a protein that carries the oxygen in the blood and allows it to be transported to cells all around the body. Haemoglobin is actually made of four units, called haem groups, each of which can carry an oxygen molecule. The success of haemoglobin can be judged by its presence in almost all vertebrates (apart from some fish), and, therefore, clearly iron's ability to form a complex with something that was made use of a long time ago in the history of life's evolution.

In some invertebrates, such as lobsters, different molecules are used, such as haemocyanin – a copper-based molecule that gives lobster blood its famous blue colour – but these creatures are much smaller and haemocyanin does not bind to blood in the same way as haemoglobin. The fact that Fe<sup>2+</sup> ions can be oxidised to Fe<sup>3+</sup> fairly easily is important to haemoglobin's success in being used across the majority of vertebrates, but other relatively common transition metal ions can also move quite easily between oxidation states, so what makes haemoglobin special? The answer is the way it manipulates equilibrium.

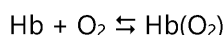
His 204

His 1

Haemocyanin  
the oxygen

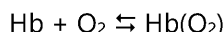
## Haemoglobin and Le Chatelier

Haemoglobin, Hb, binding to an oxygen molecule to form oxyhaemoglobin, Hb(O<sub>2</sub>), can be represented as:



The first way that Le Chatelier's principle is used is making use of the different oxygen partial pressures in the body (called partial pressures because oxygen is not the only gas dissolved in the blood). The effect of pressure affects the position of equilibrium is essentially the same as concentration. At the lungs, where the oxygen partial pressure is high, which pushes the equilibrium to the right, forming oxyhaemoglobin. As it reaches the muscles, away from the lungs, the oxygen partial pressure is much lower. This causes the position of equilibrium to shift back to the left, releasing oxygen that had been bound and freeing up the haemoglobin. The oxygen can then be used by the muscles for respiration. The oxygen can then be used by the muscles for respiration. The oxygen can then be used by the muscles for respiration. The oxygen can then be used by the muscles for respiration.

Le Chatelier's principle also explains why substances such as carbon monoxide are more strongly bound to haemoglobin than oxygen does. If carbon monoxide is inhaled, it forms carboxyhaemoglobin. The position of equilibrium for this reaction is far to the right. If carbon monoxide is inhaled, the position of equilibrium is far to the right, the concentration of free haemoglobin (Hb) is significantly reduced. The oxyhaemoglobin equation:



the equilibrium shifts to the left as haemoglobin is removed, meaning that not enough oxygen is delivered to the cells. In cells do not get enough oxygen for respiration, and a person is likely to die unless they breathe pure oxygen to push the position of equilibrium back to the right to form enough oxyhaemoglobin.

## The oxygen dissociation curve

The change in how much haemoglobin is bound to oxygen can be represented by an 'oxygen dissociation curve'. The values plotted in this curve are measured by experiment.

Towards the left of the diagram, where oxygen partial pressure is low (such as in the muscles) it is the situation where the equilibrium has shifted to the left and most haemoglobin is free (low saturation). Conversely, on the right-hand side, oxygen partial pressure is high and most haemoglobin is bound to oxygen (high saturation).

100  
95.5  
50  
0  
Percent saturation (p1, %)

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The experiment that is used to plot the dissociation curve can be carried out at different temperature or pH, in people with different health conditions or in different animals. We can find out that the shape of this curve is changed by different factors, which are altered by different factors.

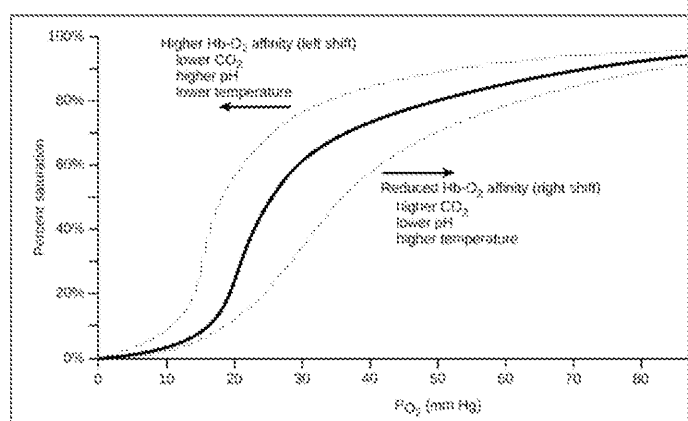


Figure 2: The effect of a change of conditions on the oxygen dissociation curve.

The shape of the curve for higher pH and lower temperature shows that haemoglobin binds oxygen more easily in these conditions. Look at the values at a 20 mmHg partial pressure of oxygen. The curve for lower temperature / higher pH has a much higher saturation of haemoglobin. This is able to carry oxygen and the position of equilibrium is shifted to the right in our blood, such as sharks, which live in cold temperatures and have a higher blood pH. This means that sharks can carry just as much oxygen in their blood, even though the oxygen pressure is lower.

This curve also shows the risk to marine life of increased CO<sub>2</sub> levels and global warming of the sea and contributes to global warming, which raises sea temperatures. This risks the occurrence of 'acidosis' in fish, whereby the shape of the oxygen dissociation curve is flattened. More oxygen is needed to saturate the haemoglobin, and it is harder for equilibrium to be shifted to the right in our lungs. Fish blood (and all blood) contains **buffers** which help minimise the change in pH. As the sea becomes more acidic. However, these buffers only work up to a certain point. Fish have to adapt to the lowering of sea pH or risk extinction as the haemoglobin in their blood is unable to carry oxygen to their muscles.

### Why is it even a curve? The cleverest bit of all...

What the shape of the curve tells us is that once some oxygen is bound to haemoglobin, it becomes easier to add a lot more (the curve becomes steeper). The reason for this is because of haemoglobin binding to oxygen – relaxed (HbR) and tensed (HbT).

- Relaxed haemoglobin binds to one oxygen molecule and becomes tensed haemoglobin (Position of equilibrium more to the left.)
- Tensed haemoglobin then easily binds to three more oxygen molecules. (Position of equilibrium more to the right.)

This is a phenomenon called **cooperative binding**. A haemoglobin molecule has four binding sites containing Fe<sup>2+</sup>. Once the first Fe<sup>2+</sup> binds to oxygen, a pull is exerted on the rest of the haemoglobin molecule (making it tensed), and moving the other three Fe<sup>2+</sup> sites into a position where they bind more easily.

This is a fantastic manipulation of equilibrium – taking a situation where the position of equilibrium lies too much to one side (like the binding of O<sub>2</sub> to HbR, with the equilibrium further to the left meaning little oxygen can be transported) and changing the situation to one where the position of equilibrium lies more in the desired direction (more O<sub>2</sub> can bind – as with HbT).

Haemoglobin  
haemoglobin

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So why not just have HbT all the time if it makes it easier to bind all four oxygen molecules? The oxygen needs to be released again at the muscles. In Figure 2, oxygen release is to the left, and the degree of saturation of Hb (y-axis) decreases. It is much harder to move the curve with a high Hb-O<sub>2</sub> affinity – the partial pressure of O<sub>2</sub> (x-axis) has to drop to a lower value for oxygen to be freed. If HbT turns back into HbR, however, HbR has a flatter curve, shifted to the right, that the oxygen is released at an earlier stage.

This is incredibly clever! The conversion between tensed haemoglobin and relaxed haemoglobin – equilibrium is truly being manipulated! Nature has fine-tuned this relationship over millions of years, and makes use of the different shapes of curves to allow more oxygen or less oxygen needs to be absorbed, or when an animal's environment changes, or pH. This ability to adapt is the basis of natural selection, and it is, therefore, not a coincidence that the position of equilibrium in different reactions has played a central role in evolution.

## Comprehension questions

1. Define the following terms:
  - a) Haem group
  - b) Partial pressure
  - c) Dissociation
  - d) Le Chatelier's principle
  - e) Buffer
  - f) Cooperative binding
2. Draw a flow diagram to illustrate what happens at each stage of the oxygen binding of Hb and release of O<sub>2</sub>.
3. Explain how acidosis can cause fish to suffocate, using the oxygen dissociation curve.
4. Write a series of bullet points to explain how haemoglobin/blood exemplifies Le Chatelier's principle.
5. Why is the ability of iron to form multiple stable oxidation states important for life?

## Application questions

6. Sketch and annotate an oxygen dissociation curve to explain the phenomenon of the Bohr effect (the opposite of acidosis).
7. How would the oxygen dissociation curve appear different if there was no cooperative binding? Why would this be a problem?
8. How would you expect the equilibrium between HbR(O<sub>2</sub>) and HbT(O<sub>2</sub>) to be affected by the Bohr effect?

## Taking it further

9. Research the different oxidation states of iron and how they link to iron's orbital configuration. Explain why iron has multiple different oxidation states.
10. What other examples of equilibrium reactions can you find in the human body or natural world that affect the position of equilibrium? Write at least half a page on your chosen example(s).

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# Rates of reaction – how not to build a mathematical model

Being able to understand and control the rates of chemical reactions is essential in swathes of industry and biology. In the body, understanding the rates of metabolism is fundamental – as is understanding the impact of conditions such as concentration on engineers designing ignition systems in car engines, which would cause the car to stop. In the finest gastronomy in France and the bridge designers working out how often their bridges will fail from the elements, people are thinking about how to make reactions faster and slower.

In the school chemistry lab, simple experiments might be done to show that an increase in a higher temperature, or that chopping up food to increase surface area allows a reaction to proceed. In the real world, however, scientists of all forms are rarely dealing with a single factor such as temperature. There must be considered if the scientists are to seize control of the exact rate of reaction. Temperature, pressure and concentration for starters.

## The rate constant

In Year 13 Chemistry, you'll meet equations that look like this:



What this means is that for the reaction on the left, where A and B react together to form P, the rate is calculated by multiplying

- k, a 'rate constant'
- [A] and [B], the concentrations of A and B. (Square brackets mean concentration)

These equations look slightly different for different reactions, especially when the rate law is not simple, but the rate is always worked out by multiplying or dividing a constant, k, by concentrations. This tells us that for a given step in a simple reaction, if we increase the concentrations of the reactants, the reaction happens faster. It also shows us that concentration is not the only thing that affects the rate.

The interesting part of this equation is the rate constant, k. It is a different number for different reactions, but it changes depending on the conditions of the reaction. An enormous value of k (e.g. for a reaction taking place in a rocket engine) means an exceptionally fast reaction. A small value of k (e.g.  $1 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  or smaller for steps in rusting) means a tortoise pace. What is the rate constant? Well, that's where the maths comes in.

### An expression

In a university textbook you may see an expression for the rate constant for a gas-phase reaction:

$$k \propto P \sigma \sqrt{\frac{T}{M}} e^{-\frac{E_a}{RT}}$$

The aim here is not to be intimidated. What this equation is saying should be understandable to an A Level student!

The first thing is to remember that an  $\alpha$  (Greek letter alpha) sign means 'proportional to'. So that the rate constant, k, is proportional to a series of factors. If you make them larger, the rate will increase and the reaction will get faster.

To understand what those factors are, a helpful trick with a complicated equation is to write it as:

So:  $k \propto P \sigma \sqrt{\frac{T}{M}} e^{-\frac{E_a}{RT}}$  becomes  $k \propto P \times \sigma \sqrt{\frac{T}{M}} \times e^{-\frac{E_a}{RT}}$

The way this has now been split up hopefully makes clear that the equation is saying that the rate constant is proportional to. These are:

- $e^{-\frac{E_a}{RT}}$  – an energy requirement
- $\sigma \sqrt{\frac{T}{M}}$  – a collision requirement
- P – a steric requirement

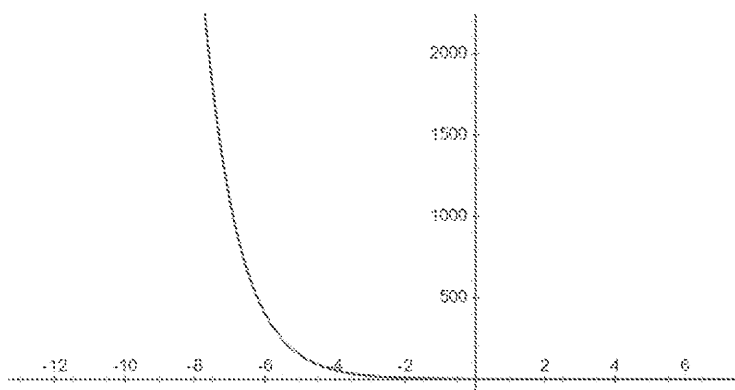
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## The energy requirement

In the expression  $e^{\frac{-E_a}{RT}}$ , 'e' is an exponential. An exponential is a particular kind of that means as one thing increases something else increases by increasing amount exponential of a negative number, which is the opposite (it decreases by decreasing it approaches 0, but never reaches 0).



A graph of  $e^{-x}$ . The curve gets closer and closer to 0 as  $x$  increases.

$e^{\frac{-E_a}{RT}}$  therefore means the negative exponential of  $E_a$  – which is the activation energy (the gas constant) and  $T$ , temperature. Does this make sense? Activation energy is the energy required for a reaction to occur. As it increases, and there is a larger energy barrier to the reaction, the rate of reaction is slower. In this expression, as  $E_a$  increases our negative exponential is going to get smaller, which does make sense. The bigger  $E_a$  is for a reaction, the smaller the rate constant for that reaction.

How is the activation energy overcome in a reaction? By increasing the temperature. This also fits with the equation because  $T$  is dividing  $E_a$ . As  $T$  increases  $\frac{E_a}{RT}$  becomes smaller, so the negative exponential  $k$  will increase. In simple terms, the higher the temperature, the faster the reaction. This portion of the equation also captures the impact of a catalyst on the rate of a reaction by providing an alternative route for a reaction with a lower activation energy. The presence of a catalyst increases the value of the rate constant  $k$  for a reaction – further reassurance that the intimate relationship between energy and rate experiences in Chemistry lessons!

## The collision requirement

For a reaction to occur, particles must collide with enough energy. The expression  $k = Ae^{-\frac{E_a}{RT}}$  includes  $A$ , which is a term in the expression that takes account of the frequency of collisions. Heavier particles will move more slowly at a given temperature, so  $M$  is in the denominator. Does this make sense? No – due to the fact that higher temperatures increase the rate constant, heavier particles will have a lower rate constant.

That leaves the curious  $\sigma$  (Greek letter sigma), which means the 'collision cross section'. This captures how easy it is for two reactant particles to hit each other – the 'target area'. The diagram to the right shows how  $\sigma$  can be represented mathematically, by looking down the path of a particle labelled A as it travels through a group of particles labelled B. Particle A has a radius of  $r_A$  and each particle B has a radius of  $r_B$ . If the distance between the centre of particle A and the centre of a particle B is less than or equal to  $(r_A + r_B)$ , the particles will collide. In other words, any particle B whose centre lies within the dashed circle will collide with A. The area of this circle is  $\sigma$  and, if we designate  $(r_A + r_B)$  as  $r$ , is equal to  $\pi r^2$ . This makes sense intuitively, with a larger molecule colliding more frequently than a small molecule travelling at the same speed, because it carves out a greater path.

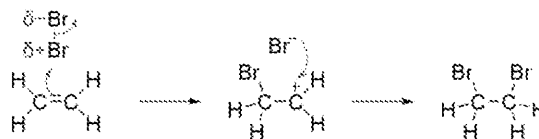


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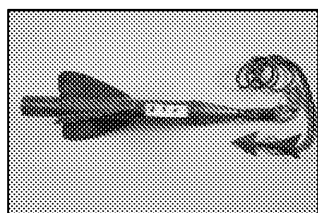


## The steric requirement

The problem with the model of the collision cross section  $\sigma$  is that it is based on particles colliding from any direction. In nearly all cases they are not, and this is where the maths breaks down. A model that takes account of the orientation of reactants is largely beyond the scope of collision theory, but fortunately the age-old solution of doing experiments provides a way out.



The example reaction above from organic chemistry provides an example of this. The bromine molecule must approach the alkene from the right direction. If it approached from the side (as does happen), the reaction would not occur. The collision cross section would, therefore, not be a circle. However, this rate of reaction at a given temperature and at given concentrations can be predicted using the Arrhenius equation:  $k \propto \sigma \sqrt{\frac{T}{M}} e^{\frac{-E_a}{RT}}$ . If we use these equations to predict the rate, we find it doesn't match experiment. The steric factor is used to calculate the unknown steric factor, given the letter P, so if the experimentally determined rate is slower than expected we would add in P to the equation for k:  $k \propto P \sigma \sqrt{\frac{T}{M}} e^{\frac{-E_a}{RT}}$ , and we would find that



By doing this, we find that, unsurprisingly, P is much less than 1. This means that many reactions are slower than expected because molecules do not have the correct orientation to react. In a fantastic example of mind-blowing chemistry, it was discovered that P was above 1 for a few reactions, such as the reaction of potassium with  $\text{Br}_2$ . This means that in some cases, atoms or ions react faster than expected. What is going on? How is this possible? The explanation is the harpoon mechanism. Potassium, K, is so keen to lose an electron that it reacts with a passing bromine molecule like a harpoon. This makes  $\text{K}^+$  and  $\text{Br}_2^-$ , which immediately react together and react (hence the name 'harpoon' – the K atom fires the electron, the

The harpoon mechanism really captures how chemistry draws together mathematical models, experimental results and creativity of thought to come up with interesting explanations of the world around us. Turns out the equations we started with are not so boring after all.

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## Comprehension questions

1. Explain what the following mean in your own words:
  - a) Rate equation
  - b)  $\alpha$  (in a mathematical context)
  - c) Exponential
2. In your own words, explain why reactions have:
  - a) a collision requirement
  - b) an energy requirement
  - c) a steric requirement
3. Using what you have learned in the article, explain why increasing the temperature increases the reaction rate.
4. Draw an illustration of the harpoon mechanism in the reaction between potassium and chlorine.

## Application questions

5. Enzymes are often large molecules which have a specific binding site that can allow them to react via a route with a lower activation energy. Suggest what energy requirement and the steric requirement for a reaction.
6. A chemist increases the temperature of a reaction by 100 Kelvin and notices a factor of 1.5. Explain why increasing the temperature by another 100 Kelvin results in a different amount.
7. The principles discussed throughout apply to gas-phase reactions. In solution, the principles need to be taken into account as a result of the solvent. Suggest reasons why the solvent would have an impact on reaction kinetics.

## Taking it further

8. Choose a real-life application of chemistry that interests you (e.g. in an industrial, medical or everyday setting) and research and write three quarters of a page on how reaction kinetics has been applied to that area.

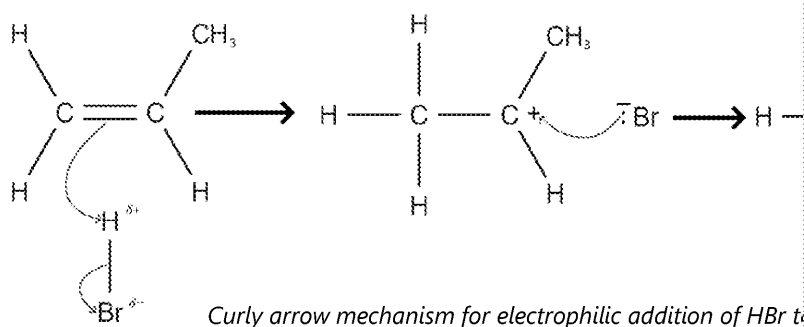
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# Expanding the chemistry of

The reaction most commonly associated with alkenes is electrophilic addition. You can use water and hydrogen halide molecules as the electrophile, but there are many possible alkenes that can undergo this reaction. This reaction is very versatile, and its use in industry is widespread. Hopefully, you are comfortable with the mechanism, outlined below.



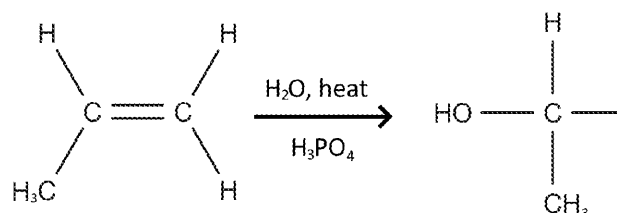
To begin with, the electron-rich carbon-carbon double bond acts as a nucleophile by donating a pair of electrons to the electron-deficient hydrogen atom in hydrogen bromide. A carbocation forms, and the H-Br bond breaks to produce a Br<sup>-</sup> ion. The Br<sup>-</sup> ion acts as the nucleophile in the second step, donating a pair of electrons to the electrophilic carbocation. The hydrogen atom is preferentially added to the less substituted carbon, i.e. the one with fewer alkyl groups attached to it. This is Markovnikov's rule, named after Vladimir Markovnikov, who published a paper on the phenomenon in 1870. Unlike the Russian chemist, we know the reason for the observation: carbocations form on more substituted carbon atoms, where they are more stable, so the hydrogen atom is left to add to the other, less substituted carbon.

displacement  
electrophile  
nucleophile

For all its importance, this type of electrophilic addition is far from the only chemical reaction involving alkenes. In this article, we will explore three further aspects of their chemistry, each of which you should expect to come to expect.

## Alkenes as nucleophiles

Electrophilic addition can be employed to convert propene into its corresponding alcohol.



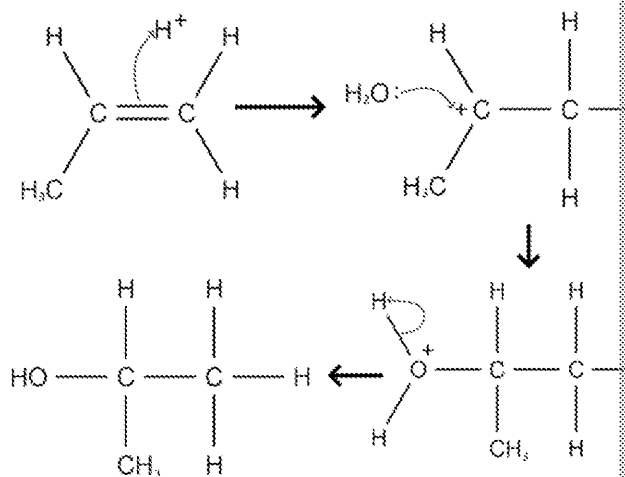
*Overview of hydration of propene*

A hydrogen atom has been added to one of the carbon atoms in the double bond, and a hydroxyl group has been added to the other. However, the hydrogen atom did not come from the water molecule, as you might expect. Instead, it was provided by the phosphoric(V) acid catalyst. Once the carbocation intermediate is formed, the water molecule acts as a nucleophile in the second step, and the acid is regenerated by picking off a proton from the oxonium ion. According to Markovnikov's rule, the major product is propan-2-ol.

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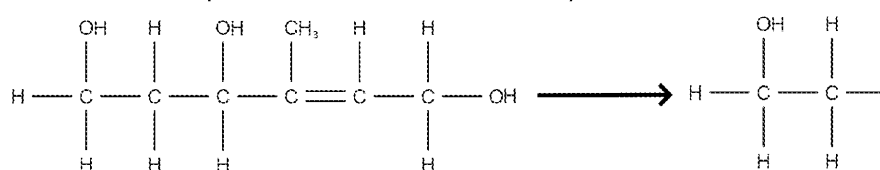
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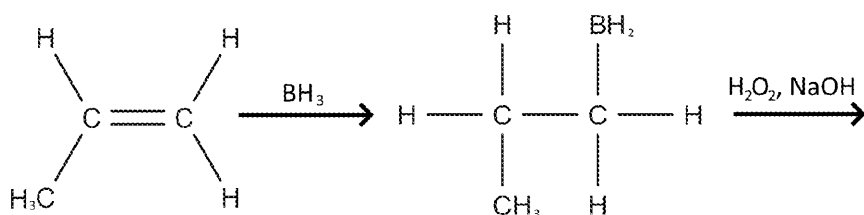
Curly arrow mechanism for hydration of propene

What if chemists want to add an OH group to the *less* substituted carbon? For example, in the synthesis of a compound with anti-tumour activity:



A step in the synthesis of a promising anti-tumour compound

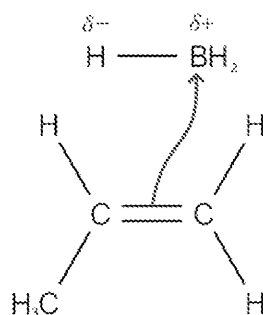
In that case, they turn to the **hydroboration-oxidation** reaction. This name makes sense because it involves two steps involved in the process.



Overview of hydroboration-oxidation reaction

During the first step, a hydrogen atom is added to one carbon in the double bond and a BH<sub>2</sub> group is added to the other (boration). Next, the BH<sub>2</sub> group is replaced by an OH group (oxidation). In this article, we'll focus on the hydroboration step, as this is where the **anti-Markovnikov** selectivity is observed.

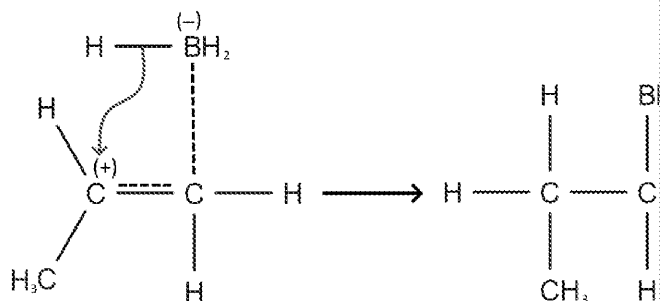
As in the two previous mechanisms, the electron-rich double bond acts as the nucleophile. When it donates a lone pair of electrons to a hydrogen atom, it attacks the boron atom. Unlike halogens, boron is *less* electronegative than hydrogen, bearing a partial positive charge. This allows the carbon to accommodate the lone pair because it only has six electrons in its outer shell, two



First step in the curly arrow mechanism for hydroboration of propene

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While this transfer of electrons takes place, a negative charge develops on the boron atom and a positive charge develops on the carbon atom. Meanwhile, a positive charge develops on the carbon atom of the double bond. Again, it is more stable on the more substituted carbon. However, once the C–B bond is formed, the electron-deficient carbon is attacked by an electrophile. Despite having no lone pairs, while the solvent molecules are too far away. What you might find surprising: the electron pair comes from one of the B–H bonds. The electrophile is an  $\text{H}^+$ , or hydride ion. Once more, this is possible because hydrogen is less electronegative than boron, allowing the lighter element to draw the electrons in the bond towards

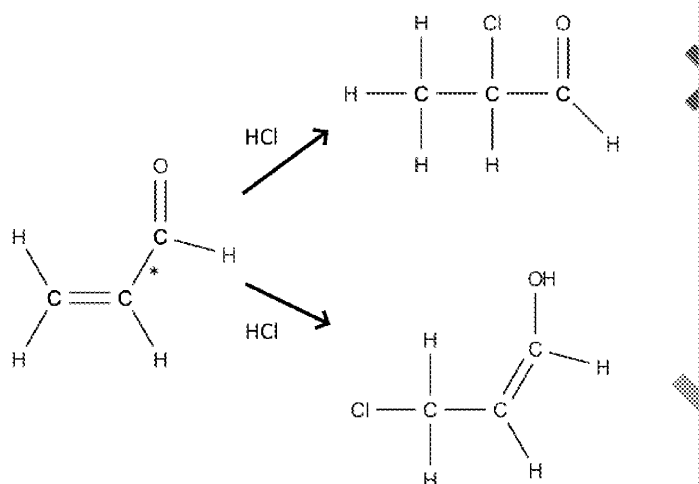


Second step in the curly arrow mechanism for hydroboration of propene; dashed line shows the case of the C–B bond) or breaking (in the case of the C–C  $\pi$ -bond); plus/minus signs above) or disappearing

With now only three bonds, the boron is neutral again, giving the expected product.

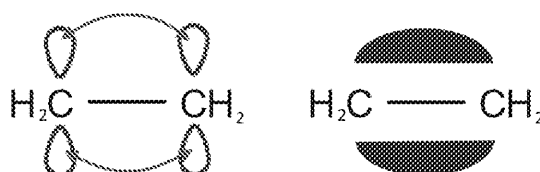
## Alkenes as electrophiles

The molecule on the left-hand side of the diagram below is called acrolein. If you consider the reaction between acrolein and HCl, you would, very reasonably, produce something on the right-hand side. In reality, the product is the bottom molecule.



Reaction of acrolein with HCl; the top product assumes the alkene is nucleophilic, the bottom product assumes it is electrophilic

If that wasn't enough, the length of the bond marked with a star is between that of a typical carbon–carbon single bond and a typical carbon–carbon double bond. What's going on? As you might know, the same is true for the C=O bond, which is probably unfamiliar. Before we get to that, let's look at ourselves of the bonding in ethene, the simplest alkene.

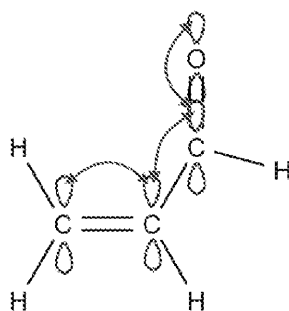


Orbital overlap involved in carbon–carbon  $\pi$ -bond (left) and the distribution of electron density (right)

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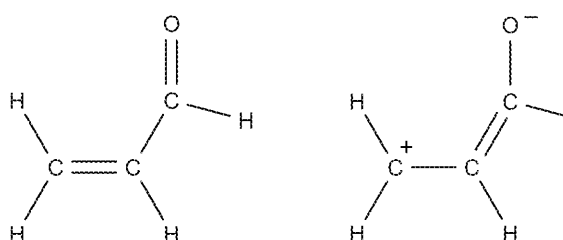
Both carbon atoms have a p orbital, which contains one electron. The two p orbitals overlap to form a  $\pi$ -bond with electron density above and below the plane of the molecule. The same is true for the C=C bond, so acrolein has two of these systems connected by a carbon-carbon single bond. In other words, rather than two, separate  $\pi$ -bonds, there is now a single  $\pi$ -system, containing



Overlap involved in  $\pi$ -system of acrolein

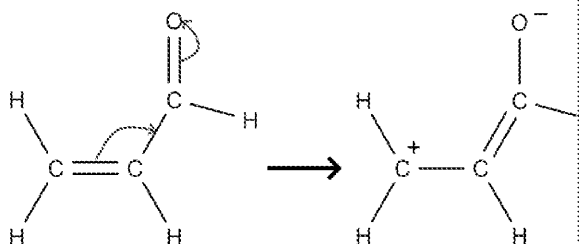
(For clarity, arrows only show overlap between top lobe of each p orbital; bottom lobe is also present)

The electrons in the  $\pi$ -system are no longer restricted to just one bond, and are so delocalised that they can be distributed across the  $\pi$  system in several ways. For instance, in acrolein:



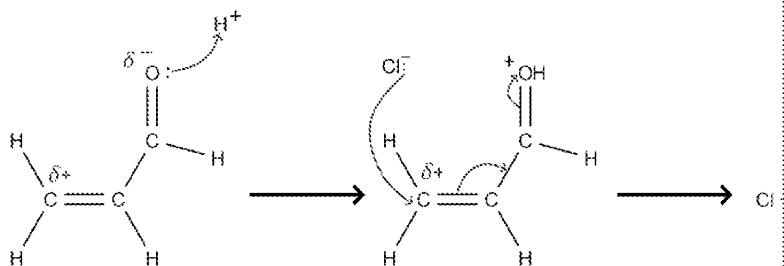
Two resonance structures of acrolein

Each of these representations is called a **resonance structure**, and can be understood as follows:



Relationship between the two resonance structures, shown using curly arrows

Even so, it is important to understand that these are *not* two different species, interconvertible by the movement of electrons. Actually, neither of them exists as shown. From experimental observations that real acrolein molecules are somewhere between these two forms – a combination of the two – the properties correspond more closely to those of the neutral structure, it is the combination of the two species that interest us. Firstly, the carbon-carbon bond marked with a star was shown to have some double bond character. Secondly, the alkene acted as an electrophile in the reaction with  $\text{HCl}$ , as the electron density was reduced by the  $\text{C}=\text{O}$  group, giving one of its carbon atoms a



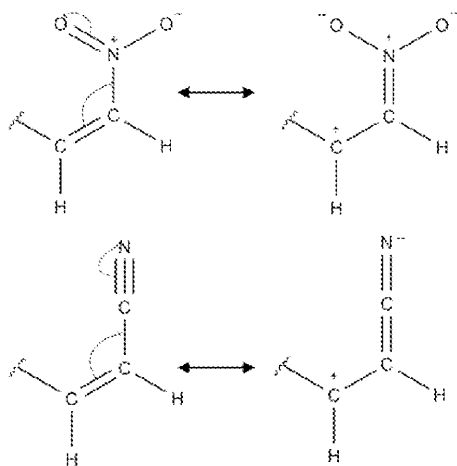
Curly arrow mechanism for the addition of  $\text{HCl}$  to acrolein

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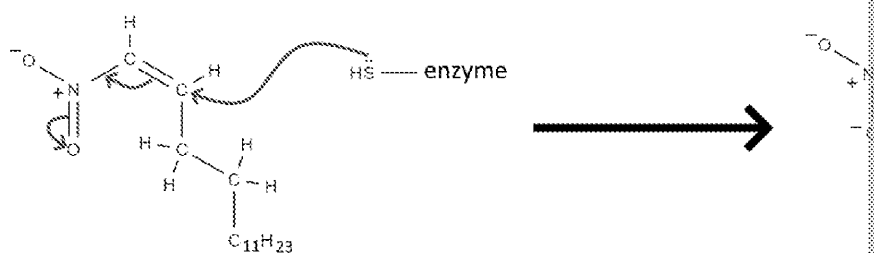


Other examples of electron-withdrawing groups include the nitro group,  $\text{NO}_2$ , and the double bonds can be separated by only one single bond; this is called **conjugation**.



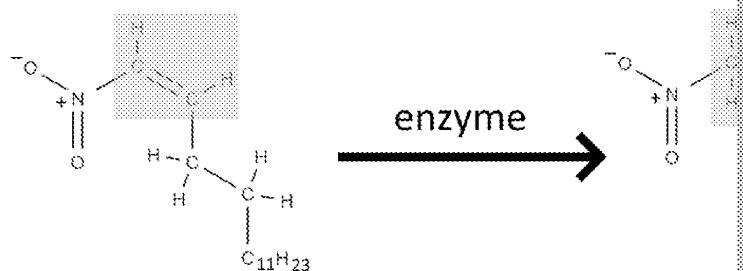
Resonance structures for an alkene conjugated to a nitro group (top) and a nitrile group (bottom). Double-headed arrows are used to link resonance structures of the same molecule.

Besides appearing in the syntheses of countless pharmaceuticals, this type of reaction is also found in nature. As an example, some termite species poison ants, their main predators, by secreting 1-nitropentadec-1-ene. The molecule wreaks havoc by reacting with various components of the ant's body, including proteins and DNA. Many important enzymes depend on a thiol group,  $\text{HS}-$ . In the reaction below, the thiol group is inactivated, preventing the enzyme from functioning.



Curly arrow mechanism for the inactivation of a thiol-containing enzyme by 1-nitropentadec-1-ene.

To avoid accidentally injuring themselves, the termites produce an enzyme that hydrolyzes 1-nitropentadec-1-ene to 1-nitropentadecane, rendering it harmless.



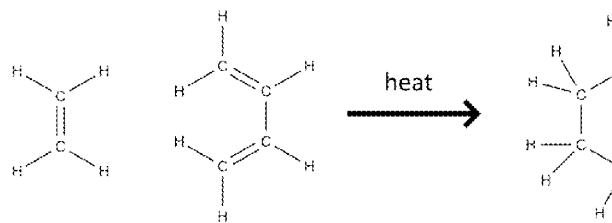
Overview of the reduction of 1-nitropentadec-1-ene to 1-nitropentadecane (situation).

## Alkenes as... neither?

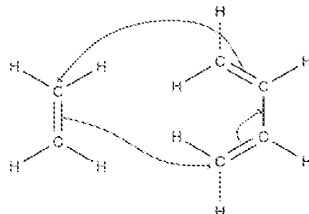
Practically all of the reactions that you will meet during your Chemistry A Level course involve electron-rich species (the nucleophile) donating a lone pair of electrons to an electron-poor species (the electrophile). Often, the mechanism will have multiple steps, and will involve charged intermediates. Exceptions are the halogenation of alkanes and, for some exam boards, the depletion of alkenes. These are radical reactions, featuring the transfer of single electrons from one species to another. The mechanism involves an initiation step, a termination step, and various propagation steps. Alkenes are often involved in a class of reactions: pericyclic reactions. An example is presented on the next page.

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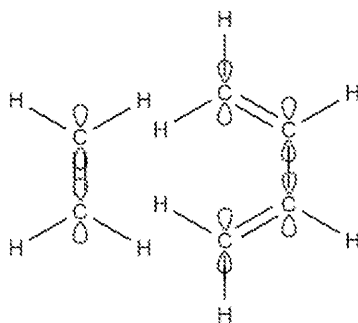


Curly arrow mechanism:



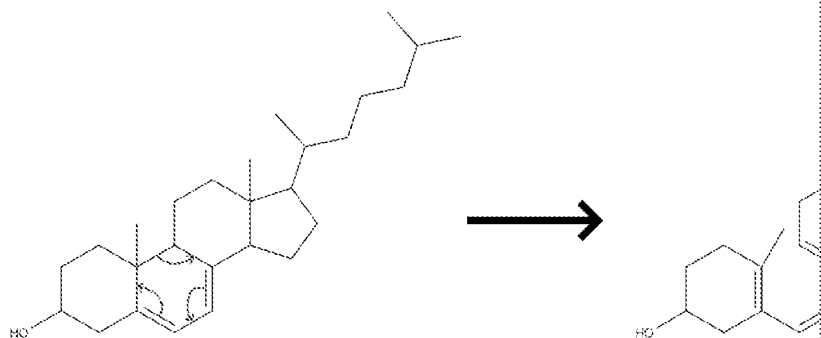
*An overview of, and curly arrow mechanism for, a cycloaddition reaction between ethene and ethyne.*

This particular type of pericyclic reaction is called a cycloaddition, as two molecules combine to form a cyclic product. Unlike polar and radical reactions, we do not have one molecule donating to another accepting it; instead, both molecules are simultaneously donating *and* accepting electrons. It would be equally valid to draw the mechanism with the directions of the arrows reversed. Other defining characteristics are that bond formation and bond breaking occur at the same time, leading directly to the product, and that the p orbitals involved are arranged in a cyclic fashion. This occurs when the reactants are exposed to certain wavelengths of light.



*The layout of the p orbitals in the cycloaddition reaction shows the cyclic nature of the reaction.*

Although pericyclic reactions are not mentioned at A Level, they are by no means unimportant. Vitamin D promotes the absorption of calcium in the bones, which is essential to human health. Vitamin D is produced in the skin by the action of ultraviolet light on cholesterol. In the autumn and winter months in the UK, most people rely on food for their main source of the vitamin. In spring and summer, however, all the vitamin D is produced in our own skin cells. Why the seasonal variation? One of the key steps in the production of vitamin D is a pericyclic reaction, and ultraviolet light from the Sun supplies the energy required for it to take place. This reaction is known as an electrocyclic ring-opening.



*Curly arrow mechanism for an electrocyclic ring-opening reaction involved in the production of vitamin D. (Due to the size of the molecule, skeletal formulae have been used.)*

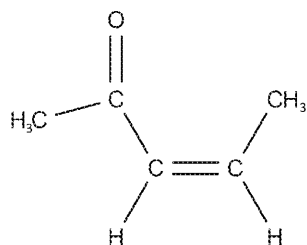
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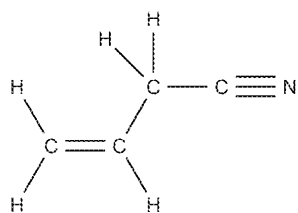


## Comprehension questions

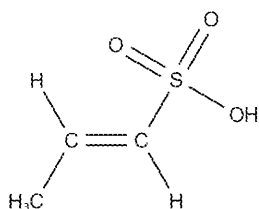
- Explain what the following terms mean:
  - Hydroboration
  - Anti-Markovnikov addition
  - Hydride ion
  - Delocalised electrons
- Explain how the properties of boron are important to hydroboration reaction.
- Predict the product of the reaction between HBr and the molecule below.



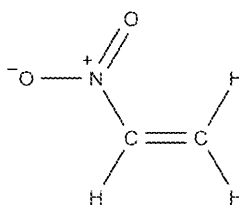
- How many of the following molecules contain an electrophilic carbon-carbon bond?



A



B

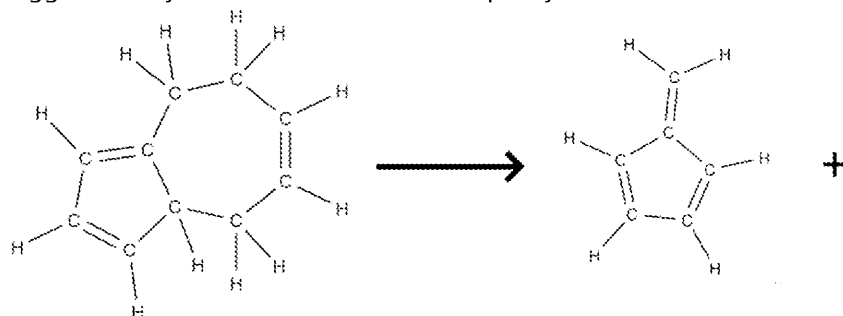


C

- How many hydrogen atoms does the vitamin D precursor in the last section contain?

## Application questions

- Look back at the product given for the reaction between HCl and acrolein. The C=C bond in this molecule is *more* nucleophilic than the one in ethene. Suggest why. (Hint: one of oxygen atom's lone pair is in a p orbital.)
- Suggest a curly arrow mechanism for the pericyclic reaction below.



(Hint: this is a cycloreversion reaction, the reverse of a cycloaddition reaction)

## Taking it further

- Alkynes are hydrocarbons that contain a carbon-carbon triple bond. Write 300 words including a comparison of their chemistry with that of alkenes.

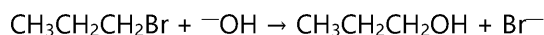
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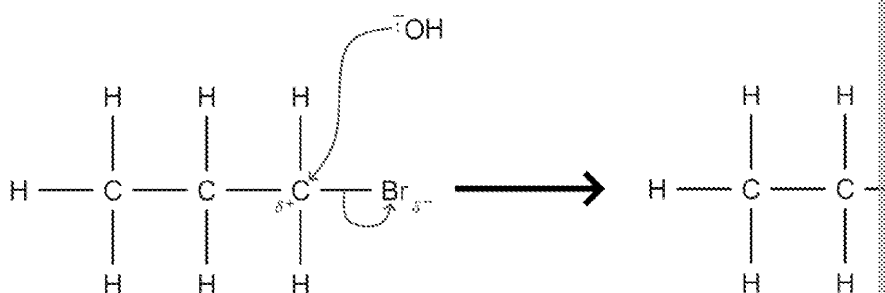


## A closer look at nucleophilic substitution

While learning about halogenoalkanes (otherwise known as haloalkanes), you will learn about nucleophilic substitution reaction. An example is presented below.



In this type of reaction, an electron-rich **nucleophile** ( $\text{OH}^-$ ) donates a lone pair of electrons to a carbon atom (the C-Br carbon), forming a bond to it and causing it to expel an atom or group, known as a **'leaving group'** ( $\text{Br}^-$ ). The overall transformation is the substitution of the nucleophile for the electrophilic carbon. You may also have covered a curly arrow mechanism for the reaction.



*Curly arrow mechanism for a nucleophilic substitution reaction*

The arrows represent visually the flow of electrons described above. The leaving group is the bromide ion. The electrophilic carbon atom cannot form five covalent bonds. (Note the partial positive charge on the carbon atom which arises from the electronegativity difference between carbon and bromine. The bromine atom being electron-deficient.)

## A diversion into kinetics

In addition to an overall equation, a reaction can be represented as a series of elementary steps. The slowest step reflects a chemical interaction, detailing which species react with each other. The curly arrow mechanism is essentially an elementary step. Where the overall equation is known, the elementary steps describe how it happens.

Among the elementary steps is a **rate-determining step**. This is the slowest step, and it acts as a bottleneck for the whole reaction. As an analogy, imagine that you are making a large fruit cake. Collecting the ingredients from the cupboard, weighing the ingredients, mixing the ingredients, leaving the mixture in the oven and decorating the cake would all be elementary steps. If the mixture needs to be left in the oven for hours, this will be the rate-determining step. Regardless of how quickly you complete the preceding steps, and how quickly you can decorate the cake, you will always be slowed down in between. Only by changing the oven's temperature can you drastically speed up the process. Similarly, the rate of a chemical reaction is dictated by the species involved in the rate-determining step.

In our nucleophilic substitution mechanism, there is only one step, so it must be the rate-determining step. It involves two species: the nucleophile and the molecule containing the leaving group. In the next paragraph, we would expect the rate of substitution to be determined by the nature of the nucleophile. Experimentally, we observe that some nucleophiles are 'good', resulting in fast substitution reactions, and others are 'bad', resulting in slow substitution reactions. The same is true for a molecule containing the leaving group.

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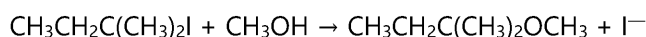
## Factors affecting the rate of substitution

Let's start with what makes a good nucleophile. This is a slightly tricky question, so we will focus on some rules of thumb. Firstly, nucleophiles donating their lone pair from a more electronegative atom are better nucleophiles (e.g.  $\text{NH}_3$  is better than  $\text{H}_2\text{O}$ ). Hopefully, this sounds reasonable. Secondly, a lone pair less tightly held will donate it more readily. Secondly, deprotonated species are better nucleophiles than their equivalent protonated species (e.g.  $\text{OH}^-$  is better than  $\text{H}_2\text{O}$  and  $\text{NH}_2^-$  is better than  $\text{NH}_3$ ).

We turn next to the molecule containing the leaving group, where we will consider two factors:

1. The leaving group – since you have only encountered nucleophilic substitution reactions involving halogenoalkanes, we will limit ourselves to halide leaving groups, which show that as the atomic radius of the halogen atoms increases down the group, the strength of their leaving groups increases, making them better leaving groups. Hence, alkyl iodides undergo substitution reactions faster than alkyl chlorides.
2. The number of alkyl groups attached to the same carbon atom as the halogen atom – due to the molecular orbitals involved in the interaction, the nucleophile must attack the electrophilic carbon from behind the leaving group. In an effect known as **steric hindrance**, the other groups bound to the carbon obstruct the approach of the nucleophile. Although the steric hindrance caused by small hydrogen atoms is insignificant, it is more pronounced with alkyl groups. As the number of alkyl groups attached to the electrophilic carbon increases from zero to three, the amount of steric hindrance increases, and the rate decreases.

At this point, we have developed a simple framework to explain the rates of nucleophilic substitution reactions. However, the reaction below seems to pose a problem.

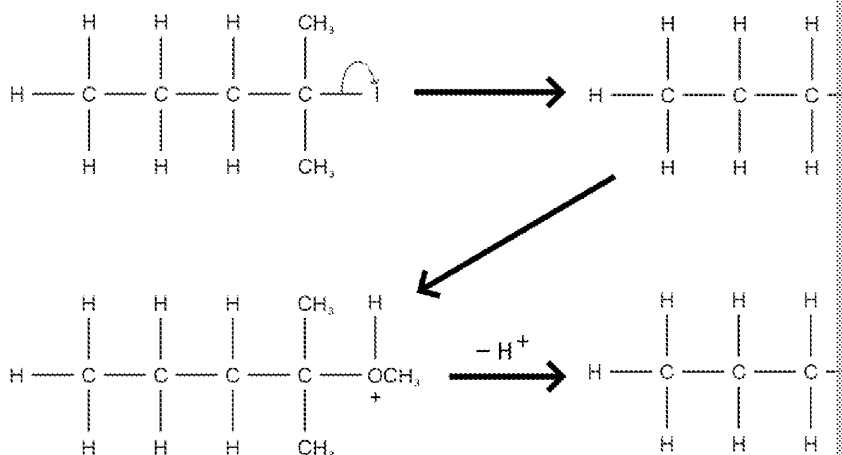


There are three alkyl groups attached to the same carbon as the iodide, severely hindering the approach of the nucleophile. Furthermore, the nucleophile is neutral, with the lone pair belonging to a neutral oxygen atom. How does substitution take place at a reasonable rate under these conditions?

The  
illustration

## The two mechanisms of nucleophilic substitution

The answer is that there is another mechanism by which nucleophilic substitution reactions can take place. The mechanism that we have been discussing so far is referred to as  $\text{S}_{\text{N}}2$ . This is because it describes the nucleophilic attack by a nucleophile, with two species involved in the rate-determining step. In the case of the reaction of methanol with tert-butyl iodide, this mechanism would be incredibly slow, for the reasons outlined. Yet, the  $\text{S}_{\text{N}}1$  mechanism is much faster. Here, while there is again a substitution reaction, only one species appears in the rate-determining step. This becomes clearer with the following diagram:



Curly arrow mechanism for the  $\text{S}_{\text{N}}1$  mechanism

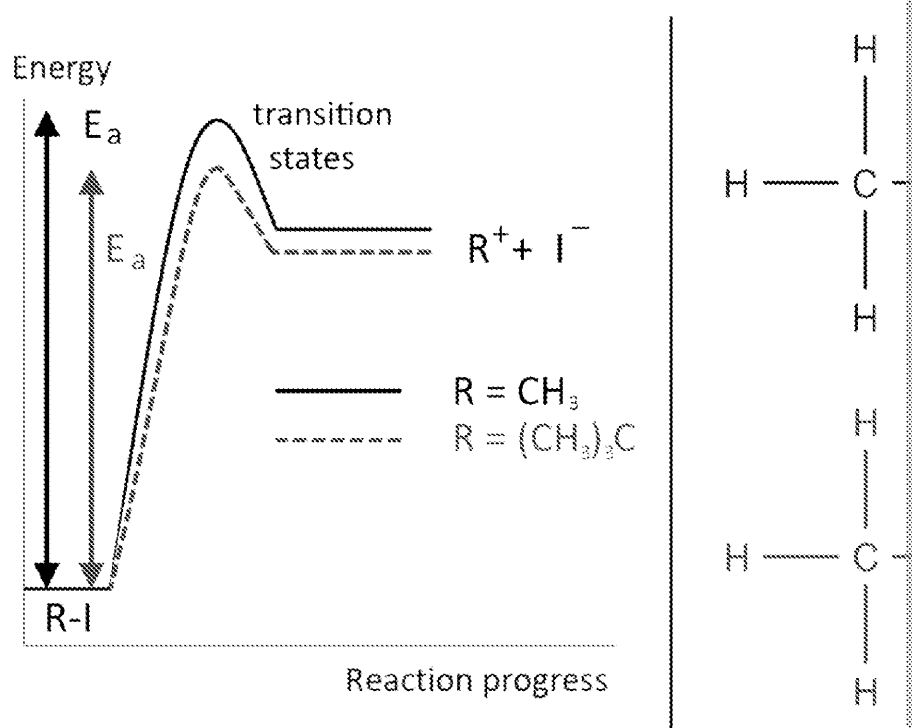
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Immediately, we can see that there are two main steps, so assigning the rate-determining step before. In the first step, the bond between the carbon and the leaving group breaks to form a carbocation intermediate. (These are also formed during electrophilic addition to an alkene.) In the second step, the nucleophile donates a lone pair to electrophilic carbocation, forming a new bond. In the third step, a proton is removed, either by a solvent molecule or by iodide, to form the final product. The first step must be rate-determining, as it is the only one that involves just one species. From a chemical sense too: a bond is being broken, leading to a high activation energy and a high energy intermediate.

The fact that the molecule containing the leaving group is the only species in the rate-determining step is perhaps surprisingly, the identity of the nucleophile is now unimportant. The carbocation is now a partial positive charge, making it very electrophilic. As a result, various species can donate a lone pair to it, including neutral solvent molecules.

Moreover, we need to re-examine what is a good structure for the molecule containing the leaving group for the  $S_N1$  mechanism, the rate of substitution *increases* as the number of alkyl groups attached to the carbon with the leaving group increases. As you discovered while studying alkenes, alkyl groups stabilise carbocations. The more alkyl groups there are connected to the same carbon, the more stable the carbocation will be as it develops in the transition state of the reaction. The more stable the transition state is, the activation energy will be lower, and the rate will be higher.



left: reaction profiles for the first step of the  $S_N1$  mechanism with  $CH_3I$  (solid line) and  $(CH_3)_2CI$  (dotted line); right: transition state for reaction with  $CH_3I$  (top) and  $(CH_3)_2CI$  (bottom); long, dotted line: bond in the process of breaking; charges in brackets represent developing charges; arrow heads on bonds indicate the direction of electron movement.

What about steric hindrance, which impedes  $S_N2$  reactions at carbons that are crowded with other groups? In  $S_N1$  reactions, the effect plays a much smaller role in determining the overall rate. With lone pairs, carbocations have a trigonal planar geometry, i.e. they are flat. Compared to the crowded transition state seen in  $S_N2$  reactions, this makes the electrophilic carbon considerably more accessible, thus minimising steric hindrance.

One factor that is key to the rate of  $S_N1$  and  $S_N2$  reactions is the identity of the leaving group. The better the leaving group, the faster the reaction. The identity of the leaving group is also involved in the rate-determining step of both reactions.

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## Closing comments

A common misconception is that, for a given set of conditions, a nucleophilic substitution reaction proceeds through only one of the two mechanisms. In reality, both are possible, and what mechanism predominates depends on the reaction conditions. When a textbook or website says that a reaction takes place through an  $S_N1$  mechanism, it means that the  $S_N1$  mechanism is significantly faster than the  $S_N2$  mechanism, and that most molecules react through this mechanism.

It should also be pointed out that, as with ionic and covalent bonding,  $S_N1$  and  $S_N2$  are not discrete mechanisms but a spectrum of mechanisms for nucleophilic substitution reactions. Cases where bond formation and bond breaking are perfectly synchronised are rare; equally, it is uncommon to see bond formation and bond breaking in a leaving group is completely broken.

Finally, you might be wondering why it matters which mechanism a nucleophilic substitution reaction proceeds through. After all, though the intermediate steps differ, the  $S_N1$  and  $S_N2$  mechanisms appear to lead to the same products. In fact, this is not true but, to understand why, you'll need to look at optical isomerism, which is covered at A2 level. Controlling this type of stereoisomerism is often a crucial aspect of drug design, especially in the pharmaceutical industry, where the optical isomer of a drug molecule can be actively toxic.

## Comprehension questions

1. Explain what the following terms mean:
  - a) Nucleophile
  - b) Rate-determining step
  - c) Carbocation
  - d) Activation energy
2. Using a table with the headings ' $S_N1$ ' and ' $S_N2$ ', compare the features of the two mechanisms: number of species in the rate-determining step, quality of the nucleophile, quality of the leaving group, how the rate depends on the number of alkyl groups attached to the same carbon atom.
3. Would you expect  $\text{PH}_3$  and  $\text{H}_2\text{S}$  to be better or worse nucleophiles than  $\text{NH}_3$ ?
4. Explain why it is rare for alkyl fluorides to undergo nucleophilic substitution reactions.

## Application questions

5. Draw the transition state for an  $S_N2$  nucleophilic substitution reaction between  $\text{OH}^-$  and  $\text{CH}_3\text{Br}$ . (Note: a bond in the process of forming is represented in the same way as a bond breaking, and a charge disappearing is represented in the same way as a charge developing.)
6.  $\text{N}_3^-$  is a much better nucleophile than  $[(\text{CH}_3)_2\text{CH}]_2\text{N}^-$ , despite both species bearing a lone pair of electrons from a nitrogen atom. Suggest why. (Hint: what shape is  $\text{N}_3^-$ ?)
7.  $(\text{CH}_3)_2(\text{CF}_3)\text{CBr}$  undergoes  $S_N1$  nucleophilic substitution more slowly than  $(\text{CH}_3)_3\text{CBr}$ . Suggest why.
8. When  $(\text{CH}_3)_3\text{CCH}_2\text{I}$  is reacted with  $\text{NaOH}$ , both nucleophilic substitution mechanisms are observed. Suggest why. (Hint: sketch the molecule.)

## Taking it further

9. Like nucleophilic substitution reactions, elimination reactions can proceed by two mechanisms,  $E1$  and  $E2$ . Research the mechanisms, then write 300 words comparing them.

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# The chemistry of vision

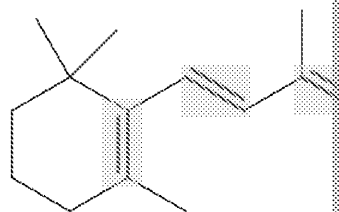
Sight is a fundamental part of life for most people. Whether crossing the street, admiring a sunset, or reading an article like this one, we are constantly being fed visual information. For many years, scientists have sought to unravel the nature of this remarkable sense. In ancient Greece, many philosophers proposed that light consisted of beams of some kind, and that, when these beams fell on an object, an image of it was formed on the eye. By the eleventh century, the Arabic scientist Alhazen had determined that visual perception was a process that occurred in the eye. Yet, it was only in the 1950s and 1960s that, thanks to advances in technology, the molecular details of sight were unveiled. In this article, we will explore these processes, including the vital role of retinal.

## A refresher on E-Z isomerism

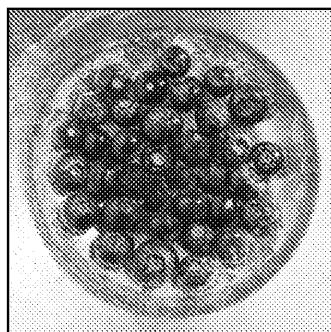
**E-Z isomerism** occurs when molecules containing a carbon-carbon double bond have two different groups attached to *both* carbon atoms in the bond. The groups can be single atoms or complex groups. If two groups on the same carbon atom, one is said to have a higher 'priority' than the other. Whichever one has the heavier atom bound directly to the carbon, e.g. OH has a higher priority than H because oxygen has a higher atomic mass than carbon. If the atoms bound to the carbon are the same, the atoms directly to *those* atoms are considered. This continues until the atoms differ. In Z isomers, the high-priority groups are on the same side of the double bond; in E isomers, they are on different sides. Carbon-carbon double bonds cannot rotate under normal conditions, preventing the interconversion of isomers. In short, this is because rotation reduces the sideways overlap between the p-orbital component of the bond. This requires the input of more energy than is available.

## The visual cycle

As you may already know, sight in humans depends on light from our surroundings striking a thin layer of tissue at the back of our eye called the **retina**. The retina contains photoreceptor cells that respond to incoming light by transmitting electrical signals to the brain, which processes the signals to produce what we experience as vision. How do these photoreceptor cells work, though? What 'switch' does light flick to trigger the electrical signals? The answer lies in a molecule called **retinal**, the key to the so-called 'visual cycle'.

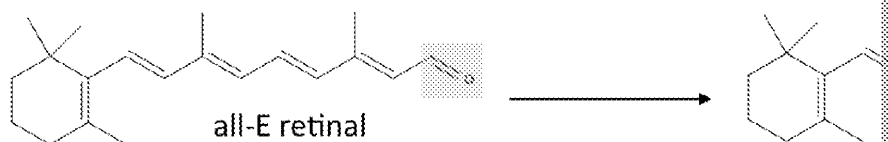


The skeletal formula of retinal highlighted in yellow and numbered.



In the diagram above, you can see that retinal contains a long chain of alternating single and double bonds. Here, the molecule is shown in its usual form, where each double bond is separated from the next by a single bond. This alternating single bond / double bond pattern is known as 'conjugation', and molecules that exhibit it often absorb visible regions of the electromagnetic spectrum. This is why they are so distinctively coloured. Examples from nature include the anthocyanins in blueberries, and the carotenoids in plants that was mentioned in the article on magnifying glasses.

Notice, too, that there is an aldehyde group at one end of the retinal's carbon chain. You learned that an aldehyde results from the partial oxidation of a primary alcohol. So, imagine that the chemistry of life is somehow different from the reactions you have learned. The relationships between functional groups are exactly the same! In fact, the first step in the visual cycle is the reverse of the process described above: the aldehyde group in retinal is reduced to an alcohol.



Conversion of all-E retinal to all-E retinol (site of change highlighted).

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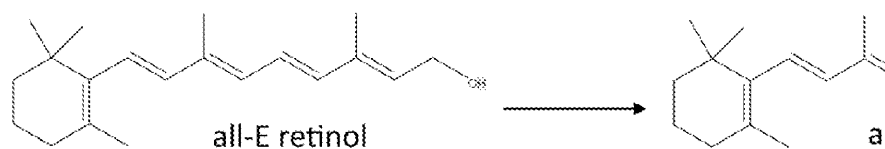
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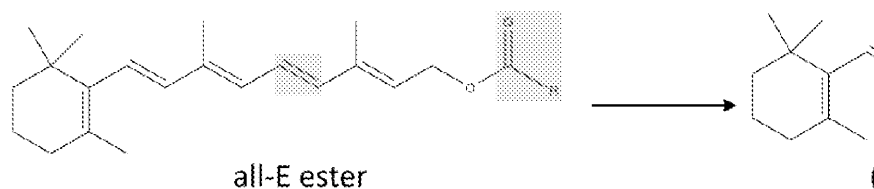
Admittedly, the reagents and conditions in nature *are* different. During your A2 s would accomplish this reduction using sodium borohydride,  $\text{NaBH}_4$ . In the aqueo reagent would react violently with the water, and our bodies instead perform the of protein that catalyses chemical reactions.

The alcohol, retinol, is then reacted with a carboxylic acid to form an ester – a fun proton in a carboxylic acid is replaced by the alkyl group from an alcohol.



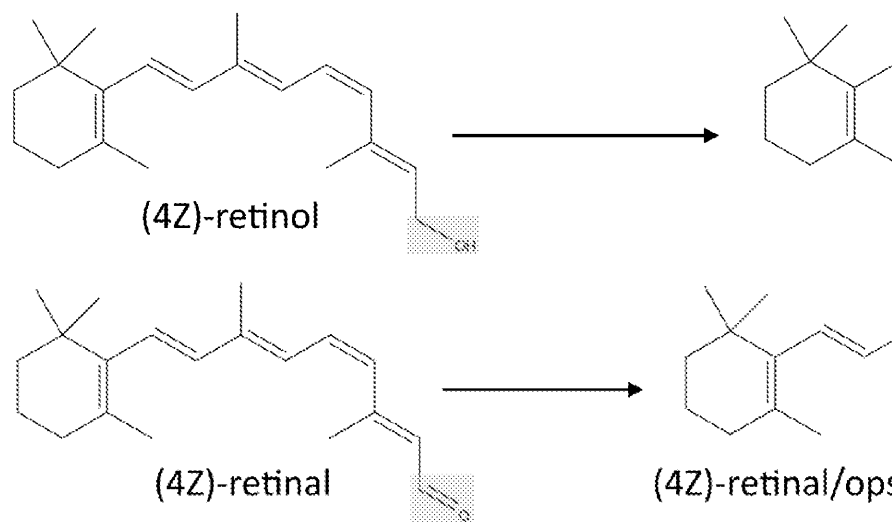
*Conversion of all-E retinol to an all-E ester (site of change highlighted); the long carboxylic acid has been abbreviated to R*

In the very next step, an enzyme breaks the ester down into an alcohol and a carb initially seem pointless. However, as part of the reaction, the stereochemistry of c is changed from E to Z. This will be important later.



*Conversion of all-E ester to (4Z)-retinol (sites of changes highlighted); the long carboxylic acid has been abbreviated to R*

Once (4Z)-retinol is oxidised enzymatically to (4Z)-retinal, only one step remains. conjugated molecules often absorbed ultraviolet or visible light? By itself, retinal For the molecule to absorb visible light, as we are expecting, it must be attached t The link is formed through the aldehyde group, and involves the smaller molecule the protein, referred to as the binding site. The structure of the binding site has e accommodate (4Z)-retinal, and fit is very tight.

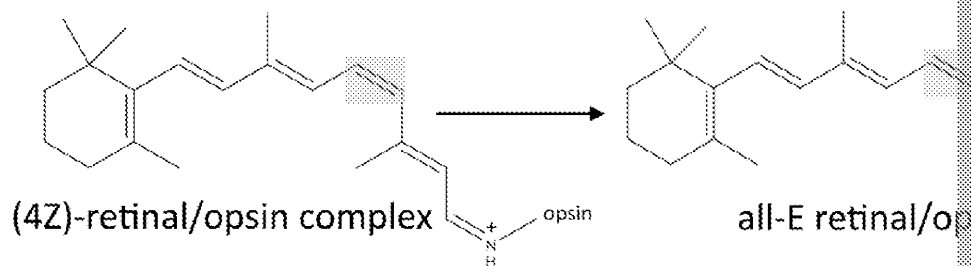


*Conversion of (4Z)-retinol to (4Z)-retinal, followed by conversion of (4Z)-retinal to (4Z)-retinal/ops (sites of changes highlighted)*

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Finally, we have our molecular switch. Now what? When a photon (a particle of light) has enough energy to break the C4–C5  $\pi$  bond, leaving the molecule free to rotate back to the all-E isomer. Since the binding pocket is arranged to specifically fit the (4Z)-retinal, it must alter to fit the new isomer. This leads to changes in the overall conformation of the protein, which is the photoreceptor cell that leads electric impulses to fire in the nervous system.



*Conversion of (4Z)-retinal/opsin complex to all-E retinal/opsin complex*

Afterwards, all-E retinal is released from the opsin binding site to begin the cycle again. The regeneration of (4Z)-retinal accounts for the dark splotches that appear in your field of vision when you step out of a dark room into bright light. With the retina flooded with photons, a large fraction of the retinal molecules are isomerised at once and, until they are replaced, your ability to see is impaired.

### Examining an old wives' tale

Were you ever told that carrots would give you night vision? It may have sounded like a trick to make you eat your vegetables, but there is some truth behind it. Interestingly, despite our reliance on it, humans cannot produce retinal. Instead, we must obtain it from our diet. As a matter of fact, retinol and retinal are more commonly known as vitamin A.

Carrots derive their striking orange colour from a conjugated molecule called beta-carotene. (The same compound is found in pumpkins and sweet potatoes.) With the help of yet another enzyme, our bodies can split this molecule into two molecules of retinal, ready to enter the visual cycle! That said, foods such as carrots only contribute to the maintenance of regular vision, and do not grant superhuman vision or the ability to see in complete darkness.

A likely explanation for this myth lies in propaganda from the Second World War. Carrots were heavily promoted to the British public, both to ensure that people were able to see during blackouts and because the vegetables could be grown domestically. Allegedly, the Air Ministry even attributed the success of their pilots to carrots, in order to distract German intelligence from the RAF's new aircraft-mounted radar systems. Before the war had ended, carrots were being endorsed by the United States government too. Over the years, these various campaigns probably gave rise to the exaggerated claims circulating today.



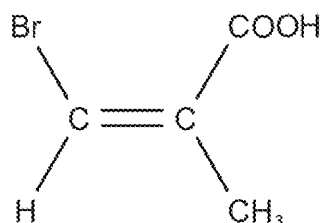
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## Comprehension questions

1. Explain what the following terms mean:
  - a) Isomer
  - b) Conjugation
  - c) Ester
  - d) Photon
2. Write the molecular formula of retinal.
3. Determine whether the molecule shown below is an E isomer or a Z isomer.



4. Explain why E and Z isomers cannot be directly interconverted without the ap

## Application questions

5. Retinal and its derivatives have to be ferried around the cell by retinoid-bind
6. Describe the reagents and conditions used in a lab to oxidise primary alcohols. Give reasons that these would not be suitable in a biological setting, such as in the
7. By considering the relative concentrations of the retinal/opsin complex and sc

## Taking it further

8. This article covered the well-established molecular mechanisms behind sight. Underpinning olfaction (sense of smell) are less certain. Research the two leading docking theory and vibration theory, and write 150 words on each of them.
9. The retinal/opsin complex is an example of a 'photoswitch', a molecule that undergoes structural change when exposed to light. Research other photoswitches, nature of their applications.

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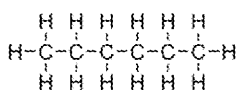
# Solvents – making solutions

When trying to improve or invent a chemical reaction a chemist will normally think about the actual chemicals that are reacting. These are the catalyst, the conditions and the area of study, and different examples of catalysts, such as metal catalysts and enzymes. The effect of conditions is an even more common area of study at school level – variables that alter the rate of reaction introduced to students at an early stage, and pH and pressure. The last of the three is often overlooked, and barely gets a mention in A Level. What makes the difference between a reaction happening and not happening. Whereas in aqueous solutions solvents are the norm, organic chemistry features a much wider selection of options. Which one to choose?

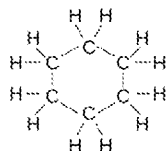
## The basics

In order to be an effective solvent, a substance needs to be able to dissolve the reactants and products during the reaction. If this doesn't happen, a reactant will simply clump together and not be able to encounter and react with other reactants. In organic chemistry solvents can be classified into two main groups:

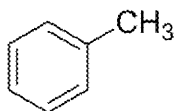
**Polar solvents vs non-polar solvents** – this refers to how much of a



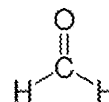
Hexane



Cyclohexane



Methylbenzene



Methanal (formaldehyde)

### Non-polar solvents

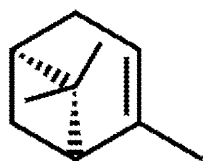
Solvents that are made entirely from carbon and hydrogen are non-polar, as there is not a sufficient electronegativity difference between the atoms to create a meaningful dipole. The principle forces between molecules are temporary dipole-dipole forces.

### Polar solvents

Solvents that have electronegative atoms or halogens bound to them are polar, so long as the molecular dipoles don't cancel out. Permanent dipole-dipole forces are present between these molecules, which are stronger than temporary dipole-dipole forces.

This difference is very useful in liquid chromatography. Molecules with long carbon chains dissolve better in a solvent like hexane, whereas a molecule with lots of oxygen atoms and a short carbon chain will dissolve better in propanone (acetone).

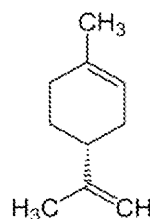
This also partly explains why oil-based foods and fatty foods often are very flavourful. Many flavour molecules are carbon-based, and often have quite similar structures. The molecules below are found in pine trees, rosemary and eucalyptus oil, whereas one of the limonene molecules is found in orange flavour, and the other a subtle lemon flavour. These molecules cannot form hydrogen bonds (or other interactions) with polar solvents, and so become concentrated in the non-polar phase.



(+)- $\alpha$ -pinene



(-)- $\alpha$ -pinene



R-limonene

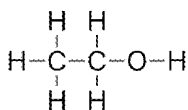
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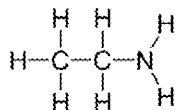


**Protic polar solvents vs non-protic polar solvents** – this refers to whether a solvent can also form hydrogen bonds.

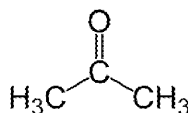
The most well-known protic solvent is, of course, water, but alcohols such as ethanol are other important examples. O–H and N–H bonds are extremely polar and the hydrogen bonds they form are extremely strong. This means that a molecule that doesn't have an O–H or N–H bond has to break apart the hydrogen bonds and dissolve. This explains why most organic molecules are not soluble in water unless they contain enough O–H or N–H bonds for their size. The larger the molecule, the more O–H or N–H bonds it needs to dissolve in water.



Ethanol (an alcohol)



Ethylamine (an amine)



Propanone (aka acetone)

#### Protic polar solvents

These solvents contain N–H or O–H bonds and can form hydrogen bonds to molecules, or can form strong interactions with ions.

#### Non-protic polar solvents

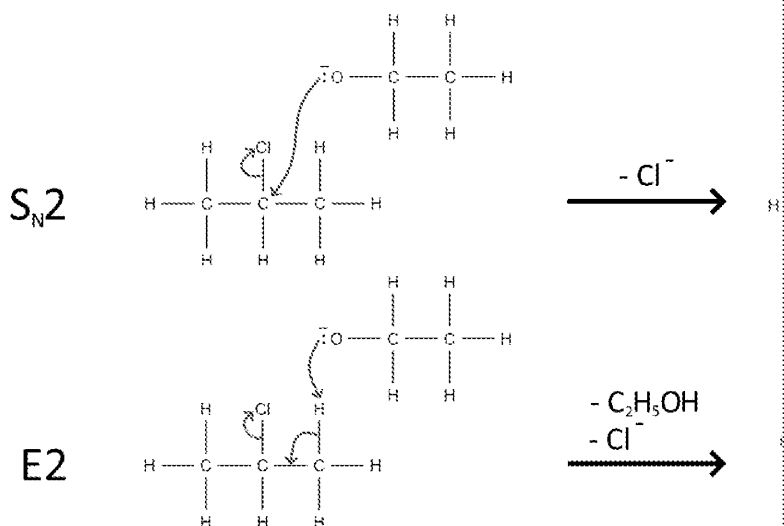
These solvents are polar and can dissolve a wider range of molecules that don't contain O–H or N–H bonds.

Caffeine is a well-known molecule that is present in tea and coffee, and has a stimulating effect on the body which is often unwanted – hence the desire for decaffeinated tea and coffee. The presence of lots of nitrogen atoms means that caffeine is polar – and it can just about dissolve in water. However, caffeine dissolves in polar non-protic solvents much more successfully. If tea is dissolved in water, and then a polar solvent is added such as dichloromethane, then the caffeine will pass into the dichloromethane, leaving the rest of the tea in the water. The water and dichloromethane can be easily separated afterwards, as they do not mix with each other (as shown in the separating funnel to the right.) This is the basis for the traditional decaffeination process – although food scientists have had to be careful not to use solvents that are harmful if they get into the tea.

*The dichloromethane is denser than water, so it sinks.*

## Effect of solvents on reactions

Consider the reaction between  $\text{CH}_3\text{CHClCH}_3$  and  $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+$ . The  $\text{CH}_3\text{CH}_2\text{O}^-$  ion is a strong base, and will carry out either an  $\text{S}_{\text{N}}2$  or elimination ( $\text{E}2$ ) reaction:



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In a polar protic solvent,  $\text{CH}_3\text{CH}_2\text{O}^-$  will be constantly surrounded by solvent molecules forming hydrogen bonds. The solvent 'shell' effectively increases the size of the ion. As discussed in nucleophilic substitution, this makes the ion less nucleophilic, and disfavours  $\text{S}_{\text{N}}2$ . In the case of  $\text{E}2$ , as the ion only needs to pick off a hydrogen atom, rather than attacking the carbon, this is less of a problem. In summary, a polar protic solvent increases the amount of the alkene product resulting from  $\text{E}2$  reactions.

On the other hand, polar aprotic solvents, being charged, dissolve better the more polar a solvent is. In a non-polar solvent, the negative  $\text{CH}_3\text{CH}_2\text{O}^-$  ions are less likely to separate, and so the  $\text{CH}_3\text{CH}_2\text{O}^-$  ion will stay together. This will inhibit *both* reactions.

## Amphiphiles

The use of organic solvents such as hexane, chloroform ( $\text{CHCl}_3$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) has been the norm in organic chemistry for decades. They work well, but there is a problem: the organic solvents ultimately derive from the processing of crude oil, which is non-renewable. Contaminated solvents must then be taken away for disposal after a reaction (as a matter of human health). It is not unheard of for a chemistry laboratory to be the biggest polluter in its locality! Over recent years, therefore, chemists have been seriously looking for alternatives to these solvents from non-renewable sources.

One innovative answer is the use of amphiphiles. An amphiphile (from the Greek words *amphi* – meaning both, *phile* – meaning like) is a molecule that has a polar protic part that dissolves in water and a non-protic or apolar part that does not dissolve in water. In water these molecules form globules called micelles (spheres) with the part that dissolves in water (hydrophilic) pointing out, and the rest of the molecule on the inside.

If the amphiphile, the organic reactants and the right choice of catalyst are added to water then the amphiphiles will form micelles, trapping the organic reactants inside with the catalyst. Once that happens, the reactants can then react in the usual way in the middle of the micelles to form products. Once the water is removed, the products can then be separated from the amphiphiles, and purified. The amphiphiles could even be reused. From a sustainability point of view this offers a much more realistic way forward for organic chemistry than the waste of gallons of solvent, and is the sort of chemistry that can win people Nobel Prizes!

Like many of science's great ideas, the concept of trapping chemical in a micelle using amphiphiles has actually been copied from nature. The idea of a biological cell is to create an environment for organic reactions to happen that would not happen in the aqueous environment outside of a cell. Many cells do this by having a bilayer of amphiphiles surrounding a cell. It's not yet totally clear how the first cell was formed, but it is a tantalising idea that amphiphiles (e.g. fatty acids and phospholipids) formed micelles in the aqueous environment of the ocean. Once they formed, they could have trapped simple organic molecules on the inside, and once they were supplied with some energy (e.g. from a thermal vent under the ocean) this could have created the environment for the first reactions that led to protein synthesis and life.



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## Comprehension questions

1. Explain what the following terms mean in your own words:
  - a) Protic and aprotic
  - b) Hydrophilic and hydrophobic
  - c) Amphiphile
  - d) Micelle
2. Why doesn't a substance bound together with hydrogen bonding mix well with dipole-dipole reactions?
3. Why can't many Bronsted-Lowry acids and bases act very well as acids or bases?
4. A chemist used an acid to catalyse an organic reaction, then added aqueous sodium hydroxide to neutralise the acid. Explain how a separating funnel can be used to remove the acid.
5. Nail-varnish remover contains propanone ( $\text{CH}_3\text{COCH}_3$ ). Suggest what this implies about the nature of nail varnish.

## Application questions

6.  $\text{Br}^-$  can act as a nucleophile in organic chemistry, and can be used in the form of sodium bromide. It does not act as a very good nucleophile if the solvent is either a) non-polar or b) protic. Explain why it cannot act well as a nucleophile in these examples.
7. A chemist wanted to separate some different halogenoalkanes using chromatography. The solvent used was one that contained the ether functional group,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ , mixed with hexane. Suggest a better choice for separating halogenoalkanes, and suggest why using pure hexane would be a poor choice.
8. If using amphiphiles to allow reactions to occur in an aqueous solvent, the size of the micelles affects the rate of the reactions happen as well as in an organic solvent. Suggest what factors affect the size of the micelles.

## Taking it further

9. Research current theories on the role of bilayers, vesicles and micelles in the cell membrane. Write a one-page summary.
10. The article contained one example of the sort of reaction that a solvent can influence. Can you research another? Explain the importance of the solvent in your own words.

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# Springing into action – the the infrared spectroscopy

Infrared (IR) spectroscopy is a useful analytical tool, commonly employed in both Despite providing less information about molecular structure than other popular t and versatile. By now, you will have learned that IR spectroscopy relies on the abs bonds, the vibrations of which in turn become more pronounced. Further details A Level syllabus, partly because of the complicated spectra generated by most org will consider simpler molecules to uncover the principles behind molecular vibrati why the spectra of larger, organic molecules are so difficult to interpret completel

## Diatomic molecules

Diatomic molecules are those that contain just two atoms, such as hydrogen chloride (HCl) and carbon monoxide (CO). Despite the difference in scale, these molecules can be modelled quite effectively by treating them like two balls connected by a stiff spring. Like a spring, the bond connecting the atoms has a resting, equilibrium length, from which it can be compressed or stretched. In fact, the bond is constantly shifting between its maximum and minimum lengths; this is molecular vibration.

A molecule can exist in one of several different vibrational energy levels, each denoted by a vibrational quantum number  $v$ . The value of  $v$  must be a non-negative whole number (0, 1, 2, 3, etc.). The higher the energy level, the further the bond can be compressed or stretched away from its equilibrium length, i.e. the greater the range of lengths. As with electrons in shells around an atom, the vibrational energy of a molecule cannot lie between energy levels, and the molecule can only move to another energy level by gaining or losing an amount of energy exactly equal to the transition energy. This occurs through the adsorption or emission of a photon. There is another restriction, too: molecules can only move to adjacent energy levels. Combining this with the fact that the separation between energy levels is much larger than the thermal energy temperature, causing them all to start in the  $v = 0$  level, the main transition in any transition. As a result, this is sometimes called the fundamental transition.

The vibrational energy of energy level  $v$  of a diatomic molecule is given, in wavenum

$$E = \left( v + \frac{1}{2} \right) \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}}$$

Some of these terms will be unfamiliar, so let's take a closer look.  $c$  is the speed of light, called the force constant and is a measure of the bond strength or, continuing the analogy, the spring. It is measured in newtons per metre ( $\text{N m}^{-1}$ ), indicating the force that is required to change the bond length by a given amount.  $k_F$  is approximately  $2290 \text{ N m}^{-1}$  for  $\text{N}\equiv\text{N}$ ,  $1130 \text{ N m}^{-1}$  for  $\text{C}=\text{C}$ , and  $500 \text{ N m}^{-1}$  for  $\text{F}-\text{F}$ . Finally,  $\mu$  is the reduced mass, measured in kilograms. This is essentially a mathematical trick to make calculations simpler. For two atoms A and B, of mass  $m_A$  and  $m_B$  respectively,

$$\mu = \frac{m_A \times m_B}{m_A + m_B}$$



Representations of a diatomic molecule when it is excited to a higher vibrational energy level.

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With definitions out of the way, we can now derive a formula for the energy of a fundamental transition:

$$\begin{aligned} E_{0 \rightarrow 1} &= E_1 - E_0 = \left(1 + \frac{1}{2}\right) \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} - \left(0 + \frac{1}{2}\right) \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} \\ &= \left(\frac{3}{2}\right) \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} - \left(\frac{1}{2}\right) \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} \\ &= \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} \end{aligned}$$

This allows us to work out, for example, the energy of the fundamental transition for a  $^{14}\text{N}^{16}\text{O}$  molecule, whose bond has a force constant of  $1595 \text{ N m}^{-1}$ . First, we will need to calculate the reduced mass of the molecule, remembering that 1 atomic mass unit equals  $1.66 \times 10^{-27} \text{ kg}$ .

$$\begin{aligned} \mu &= \frac{(14 \times 1.66 \times 10^{-27}) \times (16 \times 1.66 \times 10^{-27})}{(14 \times 1.66 \times 10^{-27}) + (16 \times 1.66 \times 10^{-27})} \\ &= 1.2 \times 10^{-26} \text{ kg} \end{aligned}$$

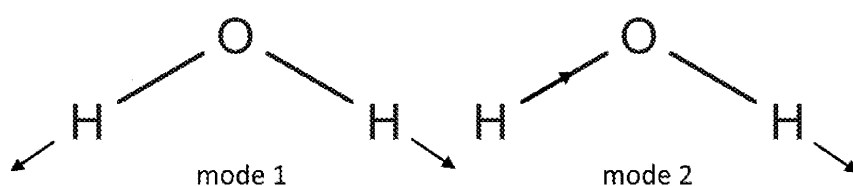
Then,

$$\begin{aligned} E_{0 \rightarrow 1} &= \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}} \\ &= \frac{1}{2\pi \times 3 \times 10^{10}} \sqrt{\frac{1595}{1.2 \times 10^{-26}}} \\ &= 1900 \text{ cm}^{-1} \end{aligned}$$

Sure enough, there is a peak at this wavenumber in the experimental IR spectrum of NO!

## Polyatomic molecules

In molecules with more than two atoms, there are multiple bonds, which can vibrate in various combinations. Chemists and spectroscopists refer to these combinations as normal modes. Normal modes can be divided into stretching modes, which involve only changes in bond length, and bending modes, which involve only changes in bond angle. A molecule containing  $N$  atoms possesses  $3N - 6$  normal modes, unless it is linear, in which case it has  $3N - 5$ . This is consistent with our previous examples of HCl and NO: they are linear and contain two atoms, giving only one normal mode, which we saw is a stretching mode. Meanwhile, a water molecule is non-linear and contains three atoms, so it displays three normal modes, represented below.



*The normal modes of water*

### Modern art

In 2003, an artist named Jeff Koons was criticised when he spent £10 million on a painting. Among the critics was the artist's own wife. A celebrated mid-twentieth-century drip technique was used to paint on a canvas in the galleries at the Tate Modern in London. The Tate Modern in London is a gallery of modern art in New York. The news of the artist's death with the help of a...

Yet, not everyone was sceptical. Some expected the painting to be a masterpiece, but a handful of scientific artists and spectroscopists were only because of the presence of a certain element. Pollock's drip technique might have cost millions of dollars...



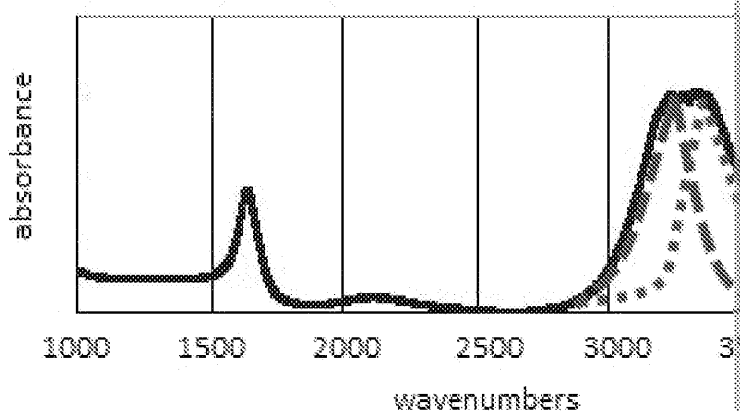
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The first two modes are stretching modes. Mode 1 is called a symmetric stretch, where both atoms are stretched and compressed at the same time; mode 2 is called an asymmetric stretch, where one atom is stretched while the other is compressed, and vice versa. Mode 3 is a bending mode, where the atoms fluctuate about its equilibrium value of  $104.5^\circ$ .

Each mode has its own value of  $\nu$  and, although the equation from the previous section can be used to calculate transition energies, we observe in spectra that each mode absorbs at a characteristic wavenumber.



An IR spectrum of water (the two stretching modes have similar transition energies, and overlap, so to show how this happens, a dashed line and a dotted line have been added to represent the two individual modes).

What about the larger, organic molecules that you are used to seeing analysed through IR spectroscopy? Applying the  $3N - 6$  formula, we discover that even a simple example like ethanol has 12 normal modes of vibration. Among those that contribute to the IR spectrum, several will have similar transition energies (in the same region), causing them to overlap, and making it difficult to assign a given peak to a specific mode. This also becomes harder to visualise as the complexity of the molecule increases.

## Limitations of IR spectroscopy

Not all normal modes can be excited by IR radiation, making it hard to identify some molecules where both atoms are the same have no IR-active modes. Think about the atmosphere:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , but not  $\text{N}_2$  or  $\text{O}_2$ !

Fortunately, normal modes that are not IR-active may show up in spectra collected through a different type of vibrational spectroscopy called Raman spectroscopy. Whereas IR spectroscopy requires the absorption of photons to reach higher vibrational energy levels through the *absorption* of photons, Raman spectroscopy involves the scattering of photons, which lose energy in the process. The incoming photons usually belong to the visible or near-visible regions of the electromagnetic spectrum. While IR and Raman spectroscopy differ in the transition energies for a given molecule, and the rules governing the transitions, they both provide complementary information about molecular structure.

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## Comprehension questions

1. Explain what the following terms mean:
  - a) Fundamental transition
  - b) Force constant
  - c) Normal mode
  - d) Fingerprint region
2. Would you expect the energy of the fundamental transition in  $^1\text{H}^{37}\text{Cl}$  to be the same as in  $^1\text{H}^{35}\text{Cl}$ ? Explain your answer.
3. How many vibrational modes does butan-1-ol have?
4. Suggest why water cannot be used as a solvent when collecting IR spectra.

## Application questions

5. Would you expect the bond in carbon monoxide (CO) to have a higher or lower force constant than the C–O bond in carbon dioxide? Explain your answer. (Hint: think about filling octets to work out the nature of the bond.)
6. Using the reduced mass and energy level transition formulae, explain why O–H stretching vibrations appear at higher wavenumbers in an IR spectrum than other bonds found in organic molecules. Why are the fundamental transition energies higher?
7. Derive a formula for the energy of the transition between  $\nu = n$  and  $\nu = (n+1)$  energy level and the one directly above it. What do you notice about your results?
8. How many stretching modes does  $\text{CO}_2$  have? Sketch them.

## Taking it further

9. Each vibrational energy level has associated rotational energy levels, describe the spacing between them. The quantum number,  $J$ . Transitions between vibrational energy levels are often accompanied by transitions between rotational energy levels. The finely spaced peaks that result from this are seen in high resolution IR and Raman spectra. Research rotational–vibrational spectroscopy and explain the following: how the spacing between rotational energy levels compares to the spacing between vibrational energy levels; the values that  $J$  can take; which transitions between rotational energy levels are allowed in IR and Raman spectroscopy; how rotational–vibrational spectroscopy can be used to identify a diatomic molecule; the P-branch and the R-branch.
10. Raman scattering is described as ‘inelastic’ because the energies of the photons are different before and after the process. On the other hand, Rayleigh scattering is ‘elastic’, with the energy of the photons remaining the same. Write 200 words, and including diagrams, explaining why:
  - i) the daytime sky to look blue
  - ii) the Sun to look yellow
  - iii) sunsets to look red

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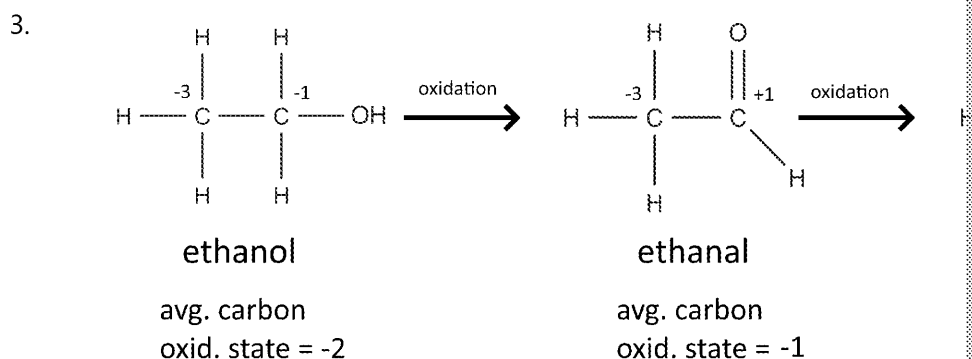


# Answers

## Redox reactions in biology

### Comprehension questions

- a) a measure of how energetically favourable a reduction process is; b) a catalyst speeds up chemical reactions; c) applies to compounds that do not contain carbon. The production of glucose from carbon dioxide using chemical reactions as a catalyst.
- a)  $\text{Hb} \cdot \text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Hb} \cdot \text{Fe}^{3+} + \text{O}_2^-$   
b)  $\text{Hb} \cdot \text{Fe}^{2+}$  is being oxidised and  $\text{O}_2$  is being reduced  
c)  $E_r^\circ = 0.33 + (-0.13) = +0.20 \text{ V}$ ;  $E_r^\circ > 0$ , so the reaction is favourable



- As explained in the article, the change in the average oxidation state of the carbon atoms in glucose, giving an overall change in oxidation state of -24.

### Application questions

- a) -1; b)  $+\frac{1}{2}$ ; c)  $-\frac{1}{3}$
- Each electron has a fixed charge, so  $E^\circ$  can be thought of as the energy taken to move a given number of electrons in a reaction. This does not depend on the number of electrons. This is an example of an **intensive** property. Another example is density. The density of a material is mass per volume, and does not vary with amount of the material present.
- a) electrolysis  
b)  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$  (reduction),  $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$  or  $\text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{e}^-$  (oxidation)

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## What are orbitals?

### Comprehension questions

- The result of waves overlapping and either adding together 'constructively' or 'destructively'. The result is an interference pattern.
  - An area of space that can hold up to two electrons.
  - The quantum number that determines the energy level of an electron.
  - The pattern which describes how an electron / an electron's probability is distributed outwards from the centre of an atom.
  - The mixing together of orbitals to form new 'hybrid' orbitals which have different shapes to the original orbitals.
  - A point where the probability of an electron existing is zero / the electron is not found.
- Own words, but should convey the idea that, for example, light or electrons (or atoms) are both waves and particles, and have properties of both. Treating them as just waves or just particles can't explain phenomena such as interference (a wave property) or having discrete energy levels (a particle property).
- See article.
- See article, but should acknowledge issues with explaining the fact that electrons are not just in one place at a particular time like a particle.
- Because s orbitals are spherical, and are, therefore, identical in every direction. p orbitals are distributed in a direction along one axis.
- Because electrons in 4s orbitals are overall lower energy than in 3d orbitals. This is due to the distribution of the 4s orbitals, which the 3d orbitals lack, and, therefore, the 4s orbitals are more spread out.

### Application questions

- 4s should have four increasing peaks, with the outer peak comfortably the largest. The 3d orbitals should be further away than the 2s and 1s orbitals in the article. 4d would be further away than 4s.
- Two of the orbitals next to each other, with the right-hand lobe (white) of one orbital overlapping with the left-hand lobe (also white) of the other.
- The large lobes of the d orbital on the left are in a particular phase (they are shaded), and the large lobes of the d orbital on the right are in a different phase (they are unshaded), so the whole orbital is in the same phase. If the d orbital overlapped with a shaded orbital (unshaded) then a  $\sigma$  bond could form. However, if the d orbital on the right overlapped with a shaded part and an unshaded part. These would not form a bond.
- Only one p orbital could form a bond as the p orbital perpendicular to the page would not overlap with the d orbital at all, and the p orbital going left-to-right has the same phase problem as the previous question.

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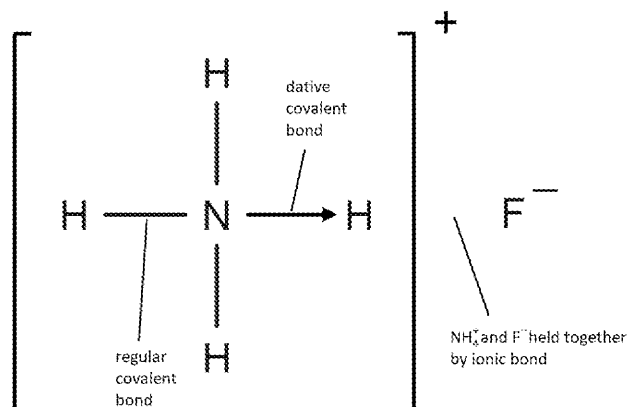


## Boron – breaking the rules of bonding

### Comprehension questions

- The ability of an element to attract a pair of electrons in a covalent bond.
  - Atoms and ions that have the same electronic configuration.
  - The probability of finding an electron in a particular area of space.
  - When the orbitals of three atoms overlap to form a bond that still only contains two electrons.
  - The idea that, for example, light and electrons have both properties of waves and particles.

2.



- Because the beryllium atom would have used both its electrons to form covalent bonds, however, it would still only have four electrons in its outer shell. It would need a second shell; therefore, it is electron-deficient.
- Nitrogen is more electronegative than boron, and, therefore, has a greater attraction for electrons in a bond. The result is that the electrons are more attracted to the nitrogen, making boron slightly positive ( $\delta^+$ ). Boron has three outer electrons and nitrogen has five, which makes it isoelectronic to Be–O as beryllium has two outer electrons and oxygen has six.
- There can be a degree of ionic attraction between slightly negative charges on oxygen and slightly positive charges on boron. This increases the strength of the bonding compared to diamond, which would theoretically make cubic boron nitride harder than diamond. The attractions are not as strong as in graphite, as the layers cannot easily slide over each other due to the charges.
- The bond angles in diborane are smaller than  $109.5^\circ$ , which is the bond angle for methane. This is because there are only four bonds round boron. This 'strain' leads to higher reactivity.
- It wouldn't be possible to plot a map of electron density if an electron was just a particle in one place at a particular time, whereas waves are spread out over a region of space, so a density map is possible.

### Application questions

- The first electron shell is much smaller than the second, third shell, etc., which means that the  $\text{H}^-$  ions would repel each other a lot more, making  $\text{H}^-$  more unstable and more reactive.
- Same as hexagonal BN (in article) but with the electron density around all the atoms being higher.
- Reducing agent – a  $3c2e$  bond is electron-deficient as the atoms have a lower electronegativity than in a normal bond (two electrons between two atoms). Therefore, a reducing agent would be able to react with a  $3c2e$  bond.

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## Magnesium – more than a silver ribbon

### Comprehension questions

- The ability to attract a pair of electrons in a covalent bond.
  - The increase or decrease in electron density as a result of a difference in dipole in a bond.
  - A solid formed from the mixing of two solutions.
  - The sum of the relative atomic masses of the atoms in a molecule.
  - A mixture of metals, usually with distinctive properties.
- Because barium ions are larger than the ions of the elements above AND large attractions to the partial negative charges on water.
- $Mg^{2+}$  ions:
  - soluble in water
  - experiences strong electrostatic attraction to oxygen and nitrogen atoms
  - relatively small
  - chemically stable, being hard to reduce or oxidiseMagnesium metal:
  - very reactive, but less so than the other group 1 and group 2 metals
  - reacts very exothermically with oxygen
  - low density
- $Mg^{2+}$  ions are soluble in water, the main constituent of cells, which also allow cell membranes. The reasons for their solubility are their high charge and small size. They experience strong electrostatic attraction to water molecules. The ions experience attraction to other molecules with oxygen and nitrogen atoms too, making them part of many important biological substances.

### Application questions

- $-1926 \text{ kJ mol}^{-1}$  is  $Mg^{2+}$  as the 2+ charge gives rise to stronger electrostatic attraction.  $-320 \text{ kJ mol}^{-1}$  is  $K^+$  as it is the largest ion (has an extra shell of electrons) meaning the attraction is the weakest (as the extra shielding outweighs the extra protons in  $K^+$ ).  $-406 \text{ kJ mol}^{-1}$  is  $Na^+$  as it only has a 1+ charge but has fewer shells than  $K^+$ , and so the attraction is stronger.
- e.g. Lithium is less dense but lithium is also more reactive.
- e.g. Low density means that the engines are lighter, meaning less fuel is needed to transport the engine.
- A cofactor is an atom, molecule or ion that binds to an enzyme and allows the enzyme to act on its substrate. (e.g. Magnesium is a cofactor for DNA polymerase.)
- A Lewis acid is an electron pair acceptor. By accepting an electron pair from the oxygen atom in the magnesium ion draws electron density away from the oxygen atom, which in turn draws electron density away from the O–H bonds, weakening them. This makes it more likely that an O–H bond will break, releasing  $H^+$  ions, which would lower the pH.

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## Haemoglobin – winning the equilibrium game

### Comprehension questions

- An iron-containing giant molecule. There are four of them in the protein.
  - The pressure exerted by one gas in a mixture of gases.
  - Splitting apart or separation of a molecule.
  - Own words, but the idea that a reaction in dynamic equilibrium will respond to change to the equilibrium.
  - A solution that minimises the change in pH when small amounts of acid are added.
  - When the binding of one molecule by a protein makes it easier for other molecules to bind.
- See article for the information that should be included.
- A lower pH causes the oxygen dissociation curve to shift to the right. This means that more oxygen is required in order to saturate the haemoglobin, meaning it is more oxygen required to its muscles.
- When oxygen partial pressure is high (e.g. in the lungs), equilibrium shifts to the right and forming oxyhaemoglobin.
  - When oxygen partial pressure is low (e.g. in the muscles), equilibrium shifts to the left and haemoglobin from oxyhaemoglobin.
  - Carbon monoxide binds strongly to haemoglobin, reducing its concentration. The equilibrium shifts to the left to restore haemoglobin concentration.
  - Buffering in the blood relies on the equilibrium  $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ . If the sea becomes more acidic, the concentration of  $\text{H}^+$  in fishes' blood increases. The equilibrium will shift to the left to reduce  $\text{H}^+$  concentration, minimising the effect of the acid.
- When iron binds to oxygen it is oxidised, and when the oxygen dissociates the iron can easily have different oxidation states it is easy for the iron in haemoglobin to have different points in the body.

### Application questions

- Diagram should be of curve shifted to the left, showing that although oxygen is bound to the haemoglobin in the lungs, the oxygen then dissociate from the haemoglobin in the muscles.
- The curve would be closer to a flat straight line. This would mean higher partial pressure of oxygen needed in order for the same amount of oxygen to bind, so it would be harder for oxygen to bind to the muscles.
- As the partial pressure of  $\text{O}_2$  increases, the equilibrium  $\text{HbR}(\text{O}_2) + 3\text{O}_2 \rightleftharpoons \text{HbT}(\text{O}_2)_3$  shifts to the right.

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## Rates of reaction – how not to be scared of mathematical models

### Comprehension questions

- Own words, but should convey the sense of an equation that describes how the rate of reaction depends on the concentrations of the reactants, raised to the power of their coefficients.
  - Own words, but essentially 'proportional to'.
  - Own words, but should convey the sense that an exponential increase in concentration leads to a much larger increase in rate.
- Reactants must collide in order to react (except in the harpoon reactions).
  - Reactants must collide with enough energy to break chemical bonds.
  - Most reactions require reactants to collide with at least one of them in a particular orientation.
- Increasing temperature increases reaction rate partly because it causes reactants to collide more frequently (see collision requirement), but mainly because it increases the proportion of collisions that meet the energy requirement.
- Open to interpretation, but should show the electron moving from K to Br<sub>2</sub> or Br<sup>-</sup>.

### Application questions

- Lowers the energy requirement as the  $E_a$  term decreases, meaning  $e^{\frac{-E_a}{RT}}$  increases. Raises the steric requirement; therefore, the steric factor decreases, reducing the rate.
- Own words but should convey the sense that the relationship with the collision frequency is additive, and that the relationship with the energy factor is exponential, not additive.
- Would affect the energy requirement as the reactants need to break the bonds of the solvent, affecting the activation energy. The collision frequency would also be affected by the rate of diffusion through the solvent, meaning that the rate of diffusion through the solvent becomes important.

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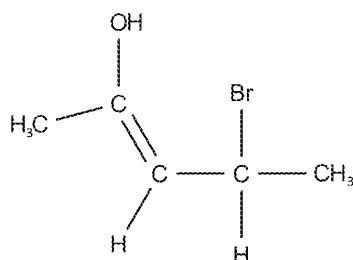


## Expanding the chemistry of alkenes

### Comprehension questions

- The addition of a hydrogen atom to one side of a carbon-carbon bond
  - Addition to a carbon-carbon double bond where the hydrogen atom bonds
  - An  $\text{H}^-$  ion.
  - Electrons that are not restricted to one bond (and/or atom).
- The fact that boron has a lower electronegativity than hydrogen means that it is more electrophilic than hydrogen on the boron atom, causing it to be attacked by the nucleophilic alkene. It is because it only has six electrons in its outer shell. The electronegativity difference between boron and hydrogen then allows the B-H bond to act as a nucleophile.

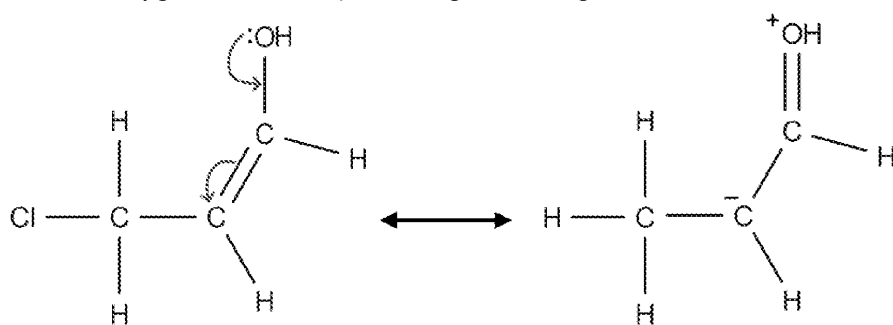
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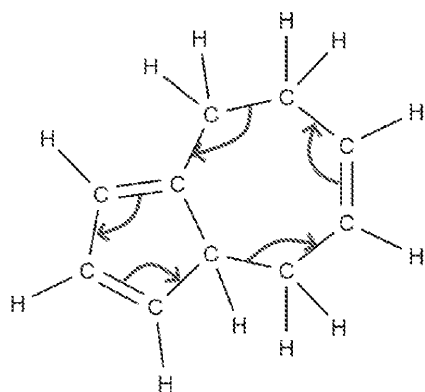
- Two; A is not electrophilic, because the carbon-nitrogen triple bond is separated from the other double bonds, i.e. the  $\pi$ -bonds are not conjugated; B is electrophilic, because the alkene oxygen  $\pi$ -bond; C is electrophilic; D is not electrophilic, because there are no  $\pi$ -bonds.
- 44

### Application questions

- The oxygen lone pair is fed into the double bond as part of a delocalised  $\pi$ -system. The carbon atom bonded to the oxygen will have a partial negative charge.



7.



(or with every arrow the opposite way round)

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## A closer look at nucleophilic substitution

### Comprehension questions

- An electron-rich species that donates a lone pair of electrons to an electrophile.
  - The slowest of the elementary steps that make up a reaction.
  - A species with a positive charge on a carbon.
  - The difference in energy between the reactants and the transition state.

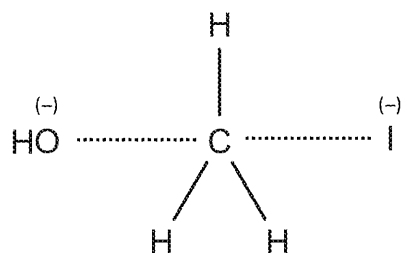
2.

	<b>S<sub>N</sub>1</b>	
<b>Number of species in the rate-determining step</b>	one	
<b>Quality of nucleophile</b>	good or bad	
<b>Quality of leaving group</b>	good	
<b>How rate depends on number of alkyl groups attached to same carbon as leaving group</b>	rate decreases as number of alkyl groups decreases	rate

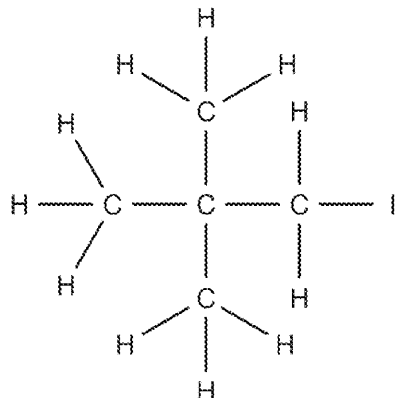
- PH<sub>3</sub> and H<sub>2</sub>S should be better nucleophiles than NH<sub>3</sub> and H<sub>2</sub>O, because phosphorus is more electronegative, on account of being further down their respective groups.
- C–F bonds are strong, making F<sup>–</sup> a bad leaving group.

### Application questions

5.



- [(CH<sub>3</sub>)<sub>2</sub>CH]<sub>2</sub>N<sup>–</sup> has two bulky alkyl groups attached to the nitrogen atom, so it has a lot of steric hindrance. Meanwhile, N<sub>3</sub><sup>–</sup> has a sleek, linear shape, minimising steric hindrance.
- Due to their high electronegativity, the fluorine atoms in the CF<sub>3</sub> group remove electron density from the carbon, destabilising the developing positive charge in the transition state, increasing the activation energy, and a slower rate.
- S<sub>N</sub>1 is slow because there is only one alkyl group attached to the same carbon. There is little stabilisation of the developing positive charge in the transition state. Alkyl groups on the adjacent carbon to the leaving group lie along its path of attack.



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## The chemistry of vision

### Comprehension questions

- One of multiple molecules with the same molecular formula but a different structure.
  - The presence of alternating single and double bonds in a molecule.
  - A class of molecules containing the  $\text{RCO}_2\text{R}'$  functional group.
  - A single particle of light.
- $\text{C}_{20}\text{H}_{28}\text{O}$
- Z isomer. The first atom in each group attached to the right-hand carbon is a bromine atom. What is bonded to those carbons. Oxygen has a higher atomic mass than hydrogen. It is on the same side as the bromine.
- Carbon-carbon double bonds contain a  $\pi$  component formed by sideways overlap of  $2p$  orbitals. In order to switch between geometric isomers, one of these orbitals must rotate to the other. At the point where the orbitals are perpendicular, there is no overlap and the  $\pi$  bond breaks. This requires the input of more energy than is available at room temperature.

### Application questions

- Most of the retinal molecule is composed of carbon and hydrogen, rendering it insoluble in the water that comprises much of a cell's interior. This problem is solved by attaching it to water-soluble proteins.
- Oxidation of alcohols is carried out by heating them with acidified potassium dichromate(VI). A problem is that high temperature and low pH could damage cells; by denaturing them. Secondly, the dichromate(VI) ion is toxic and carcinogenic.
- In daylight, photoreceptors are constantly being struck by photons, meaning that the retinal/opsin complex is inactive at any given time. Thus, the probability of any given photon that enters the eye striking a retinal/opsin complex is lowered. In the dark, there are far fewer photons, and therefore fewer retinal/opsin complexes. When a photon enters the eye, the likelihood of it striking a retinal/opsin complex is higher.

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## Solvents – making solutions!

### Comprehension questions

- Own words but protic = a solvent that can form hydrogen bonds, aprotic does not form hydrogen bonds.
  - Attracted to / repelled by water.
  - A molecule with hydrophilic and hydrophobic parts.
  - A sphere formed when amphiphilic molecules group together, creating a hydrophobic interior.
- Hydrogen bonds are stronger than dipole–dipole interactions. In order for the hydrogen bonds to be broken and replaced with dipole–dipole interactions, which are weaker, hydrogen bonds are stronger.
- In a non-polar solvent, ions cannot mix well with the solvent, and, therefore,  $\text{H}^+$  ions cannot be released easily by acids).
- The organic products are most likely to dissolve better in an organic solvent than in water. If the chemist pours the reaction into a separating funnel at the end of the reaction, the aqueous base will form one layer and the organic solvent with the product will form another. After shaking/inverting and allowing the layers to separate, the tap in the separating funnel is used to collect the bottom layer, leaving the other layer (usually the organic layer) in the top.
- They are polar and aprotic.

### Application questions

- $\text{NaBr}$  cannot easily separate to form ions.
  - The protic solvent forms strong attractions to the  $\text{Br}^-$  ion charge, meaning it cannot easily get to another molecule to act as a nucleophile.
- The ether is polar, due to the oxygen, but is not protic as there is no O–H bond. Halogenoalkanes, which are also polar and aprotic.
- Lots of answers, including size and shape of the hydrophilic and hydrophobic parts, how polar the hydrophilic parts are (which will affect the strength of attraction), therefore, how tightly they pack together). External factors include temperature, the nature of the molecules, and pH, which will affect how attracted the hydrophilic parts are to water. Concentration will also be important as micelle formation can be an equilibrium.

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## Springing into action – the theory behind infrared spectroscopy

### Comprehension questions

- the transition between  $v = 0$  and  $v = 1$ ; b) a measure of the strength of a force required to extend or compress by a given amount; c) the simultaneous combination of bonds in a molecule; d) a complicated region of an IR spectrum between  $1500\text{ cm}^{-1}$ , with large numbers of overlapping peaks that are difficult to interpret
- The reduced mass of  $^1\text{H}^{37}\text{Cl}$  is higher than that of  $^1\text{H}^{35}\text{Cl}$ . As the energy of the transition is proportional to  $\frac{1}{\sqrt{\mu}}$ , it would be smaller for  $^1\text{H}^{37}\text{Cl}$ .
- Butan-1-ol has 15 atoms and is non-linear;  $(3 \times 15) - 6 = 39$  normal modes
- Water strongly absorbs IR radiation, meaning that it would appear in an IR spectrum as a set of very strong, broad, and often overlapping peaks, obscuring other peaks from the molecule under study, complicating analysis.

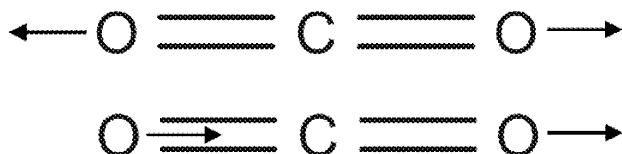
### Application questions

- $\text{O}_2$  has a double bond, while  $\text{CO}$  has a triple bond. A triple bond is stronger than a double bond, so the vibrational frequency is higher for  $\text{CO}$ .
- $$E_{n \rightarrow n+1} = \frac{1}{2\pi c} \sqrt{\frac{k_F}{\mu}}$$

The expression is independent of  $n$ , i.e. all vibrational energy levels are evenly spaced. Therefore, we expect all transitions to appear on top of each other in a spectrum.
- When  $m_A$  is much bigger than  $m_B$  (as in the case of N or O bonded to H),  $m_A + m_B \approx m_A$  ( $\approx$  means 'is approximately equal to')
 
$$\mu \approx \frac{m_A \times m_B}{m_A}$$

$$= m_B$$

Since  $m_B$  is small,  $\mu$  is small. This leads to a high vibrational transition energy.
- Two (a symmetric stretch and an asymmetric stretch)



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